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RESIDUAL MANAGEMENT BY LAND DISPOSAL

Proceedings of the Hazardous Waste Research Symposium

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A research symposium was held to exchange recent information on land disposal of municipal and hazardous wastes. Papers were presented and compiled into a report on the following topics: (1)Case studies of actual and potential environmental impact from land disposal of hazardous wastes; (2) Technology of preventing adverse environmental impact; (3) Selection of disposal sites to minimize adverse impact; (4) Ameliorating damages at existing disposal sites and suggested modification of future sites and wastestreams; (5) Identification of pollution potential of selected industrial solid wastes, and (6) Special disposal problems.

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DEVELOPMENT OF A COMPUTER SIMULATION MODEL FOR PREDICTING TRACE ELEMENT ATTENUATION IN SOILS[1]

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The University of Arizona
Tucson, Arizona 85721

ABSTRACT

Columns of differing soils were leached with various trace metals so as to obtain breakthrough curves. A nonequilibrium model presented by Lapidus and Amundson was applied to the data obtained from these short term laboratory soil columns. The data was used to obtain the dispersion coefficient and first order rate constants assumed in the model. This was done via a nonlinear parameter estimation procedure using a standard least squares gradient technique. The parameters were then used to obtain "time of travel" curves which were generated for long times. Such curves can easily be used in formulating design criteria for the management of trace metal migration in soils.

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[1] Original paper in the final draft of Report submitted to Solid and Hazardous Waste Research Division, Municipal Environmental Research Laboratory, U.S. Environmental Protection Agency, for Contract No. 68-03-0208, March 1976, Cincinnati, OH 45268, (In press).

[2] Current address, Soil Science, University of Wisconsin, Madison.

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FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communiciations link between the researcher and the user community.

The proceedings identify research aimed at minimizing the impact of disposing of hazardous wastes directly to the land and provides solutions to unique problems.

Francis T. Mayo
Director
Municipal Environmental
Research Laboratory

PREFACE

The proceedings are primarily intended to disseminate information on extramural research projects funded by the Solid and Hazardous Waste Research Division (SHWRD) of the U.S. EPA, Municipal Environmental Research Laboratory in Cincinnati, Ohio. Selected papers from the programs of other organizations were included in the symposium either to identify closely related work not included in the SHWRD program or to present an alternative approach to a problem.

The symposium and the resulting proceedings have two objectives: (1) to disseminate information from ongoing and recently completed SHWRD projects in a timely fashion and (2) to bring together people who share common interests and who can benefit from an exchange of research information and views.

Discussion of research projects on an interim basis provide data and information that could be used by other researchers and the hazardous waste management industry. The symposium provides a forum for these interim discussions.

Papers in this proceedings are grouped as they were presented in the sessions during the symposium. These groupings correspond to improtant aspects of disposal research and reflect, we think, major areas of interest for government, university, and commercial personnel engaged in hazardous waste management or research.

The first session, "Introduction and Orientation," presented an overview of Federal research and legislative development programs for hazardous waste disposal.

The second session, "Identification of Pollution Potential," dealt with techniques for gathering and interpreting information about problems with disposal of hazardous wastes. Generally, the papers in this session support the need for a program of disposal research and outline some of the methods currently being used to gather data on adverse environmental impacts from land disposal of hazardous wastes.

The third session, "Modification of Disposal Sites and Waste Streams," discussed some presently available techniques for dealing with potential disposal problems. Papers in this session focused on preventing the release of contaminants from the site by chemically altering the waste or the soil and by installing impervious liners. Additionally, there was discussion of using naturally secure environments such as salt mines for storage and disposal of hazardous wastes.

The fourth session, "Special Disposal Problems," described studies of specific wastes which are "special" because they are either unusually concentrated or contain substances that are hazardous in very low concentrations. Although several of the studies were specific to one waste, the results are applicable to other types of waste that were not studied. For example, the work on hexachlorobenzene, vinyl chloride, and pesticides will be useful in solving the general problem of organic waste disposal on land.

In the last session, "Predicting Trace Element Migration," a series of papers were presented on predicting how contaminants will move in a specific soil and waste. In addition to discussing predictive and modeling procedures, the papers covered techniques and problems of detecting contaminant movement in soils and of determining the soil properties and contaminant characteristics which control this movement.

Because knowing how contaminants will move in a given situation is the starting point for solving the problem of selecting safe land disposal sites, there was much interest in this area of work. It is not surprising that there were also some pronounced differences of opinion about the most effective way to model or predict contaminant movement in soil and about the relative importance of soil properties in controlling the rate of movement. We think these differences of opinion are a reflection of the complexity of the soil-waste system and of the rapidly developing state-of-the-art of dealing with this difficult problem. Resolution of these differences is expected as work progresses and, particularly, as conclusions based on laboratory studies are tested against field data.

The papers are printed here as received from the authors and do not necessarily reflect the policies and opinions of the U.S. Environmental Protection Agency or the management of this station. We hope that the printing of these proceedings will enable a wider audience to benefit from the information available and that these proceedings will stimulate interest in developing safer methods of hazardous waste disposal on land as well as increased participation in subsequent symposia on this topic.

ABSTRACT

A research symposium was held to exchange recent information on land disposal of municipal and hazardous wastes. Papers were presented and compiled into a report on the following topics:

1. Case studies of actual and potential environmental impact from land disposal of hazardous wastes;
2. Technology of preventing adverse environmental impact including: (a) processing waste prior to disposal and (b) modification of disposal sites and management of disposal operations;
3. Selection of disposal sites to minimize adverse impact;
4. Ameliorating damages at existing disposal sites and suggested modification of future sites and wastestreams;
5. Identification of pollution potential of selected industrial solid wastes, and
6. Special disposal problems.

The presentations were grouped for convenience into five half-day sessions under the topics of:

1. Current research (SHWRD) and demonstration projects (OSWMP) on land disposal and disposal standards and criteria documents involving hazardous wastes;
2. Identification of pollution potential of solid and hazardous wastes;
3. Modification of disposal sites and waste streams;
4. Disposal problems of special industrial hazardous wastes; and
5. Predicting trace element migration through soils.

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CURRENT RESEARCH ON LAND DISPOSAL OF HAZARDOUS WASTES

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ABSTRACT

The Solid and Hazardous Waste Research Division (SHWRD), Municipal Environmental Research Laboratory, U.S. Environmental Protection Agency, in Cincinnati, Ohio, has responsibility for research in the areas of solid and hazardous waste management, including both disposal and processing. This research is being directed towards new and improved systems of solid and hazardous waste management, development of technology, determination of environmental effects, and collection of data necessary for the establishment of processing and disposal guidelines. In the past, the Division concentrated on problems associated with municipal solid wastes, but over the recent years the emphasis has shifted more toward hazardous waste management, and disposal alone and in combination with municipal wastes.

SHWRD has divided its hazardous waste research program into two general areas: (a) Disposal of Hazardous Residuals to the Land, and (b) Hazardous Waste Materials Treatment. This paper will discuss the overall hazardous waste research program, realizing that this research symposium is primarily directed toward the land disposal aspects of hazardous residuals. SHWRD has basically classified its current hazardous waste research program into six categorical areas shown below:

1. Identification and Characterization of Hazardous Waste
2. Hazardous Waste Decomposition
3. Pollutant Migration Through Soils
4. Control Technology
5. Specialized Wastes
6. Alternatives for Hazardous Waste Landfills

INTRODUCTION

Increasing amounts of hazardous and toxic wastes are being directed to the land for disposal by landfilling. At the same time, there is increasing evidence of environmental damage resulting from improper operation. The burden of operating landfills and coping with any resulting damages falls most heavily on municipalities and other local government agencies. Their problems are complex, involving legislation, economics, and public attitudes as well as technology; additionally, comprehensive information on how to landfill and protect the local environment is not readily available.

Part of the long range solution to this problem will be design and operation manuals, to be published by the Municipal Environmental Research Laboratory, describing recommended procedures and technology for minimizing the impact from landfilling of strictly municipal wastes as well as hazardous and toxic wastes. Although these manuals will not be published until about 1980, a series of intermediate reports will be published, detailing present and future research findings that will be incorporated into the final design and operation manuals. This paper describes seven current projects supporting the development of these manuals.

IDENTIFICATION AND CHARACTERIZATION OF HAZARDOUS WASTES

Environmental Effects Documents

This research (1) is being performed to provide human health and environmental effects as they may relate to the management and land disposal of selected hazardous substances/wastes, thus providing a data base that summarizes, assesses, and interprets health and ecological effects of specific hazardous wastes. The hazardous waste environmental effects documents will contain:

Comprehensive effects data for:

--all forms of life, both human and other living organisms, for the air, water, and land

Environmental aspects of hazardous materials for:

--environmental distribution
--transport through soil; through soil to water or air; and through water or air to humans or other organisms
--transformation
--fate
--accumulation and magnification

These documents are currently being developed for the following hazardous materials and related compounds:

arsenic
asbestos
benzidine
beryllium
cadmium
chromium
cyanides
endrin
fluorides
lead
mercury
methyl/parathion
PCB's
toxaphene

Several previous reviews* of these efforts have been presented.

Standard Sampling Techniques

Standard sampling procedures (2), including collection, preservation, and storage of samples, do not exist for solid and semi-solid wastes. Hazardous wastes, both at the point of generation and the point of disposal, are not homogenous mixtures and, additionally, may range in consistency from a liquid, through a pumpable sludge, to a nonpumpable solid. Existing procedures for sampling liquid effluents and soils will have application but must be adapted to a variety of circumstances and, more importantly, field tested extensively before they can be advocated as "the" way to sample. Experience with sampling procedures is being accumulated as part of several on-going SHWRD projects and our initial effort in this area relates to the chemical composition, physical characteristics, and origin of hazardous wastes delivered to several Class I (hazardous chemical) landfills in the State of California.

Standard Analytical Techniques

Assuming that a representative sample can be taken from a hazardous waste, the next problem is to analyze the waste. Existing instrumentation functions well on simple mixtures at low concentrations but encounters interference problems with complex mixtures containing materials at high concentrations (a percent by weight and greater). In this range the sample cannot be analyzed directly but must be diluted. Options here are the development of standard procedures for diluting and accounting for errors introduced thereby or, development of instrumentation capable of accurate, direct measurements at high concentrations in the presence of potential multiple interferences. Existing EPA procedures for drinking water and liquid effluents are often not applicable. Analytical procedures are being developed on

*Schomaker, N. B., and Roulier, M. H., Current EPA Research Activities in Solid Waste Management: Research Symposium on Gas and Leachate from Landfills: Formation, Collection and Treatment. March 25-26, 1975, Rutgers, State University of New Jersey.

an as-needed basis as part of the SHWRD projects. However, most of this work is specific to the wastes being studied and a separate effort is required to ensure that more general procedures/equipment will be developed. A compilation of analytical techniques (2) used for hazardous waste analysis is planned for award later this fiscal year.

Standard Leaching Techniques

Because environmental impact cannot occur until contaminants are released from a waste, a standard leaching test is needed to assess potential contaminant release from a waste. Such a test must provide information on the initial release of contaminants from a waste when it is contacted not only with water but with other solvents which could be brought for disposal. Additionally, such a test must provide some estimate of the behavior of the waste under extended leaching. Experience from on-going SHWRD projects indicates that some wastes may initially release only small amounts of contaminants but, under extended leaching, will release much higher concentrations. Such leaching behavior has an impact on disposal regulation and on management of a disposal site and information on this behavior must be obtained as part of the process of classifying a waste. The Office of Solid Waste Management Programs (OSWMP) has funded an Industrial Environmental Research Laboratory (IERL) project (3) to examine this area and develop procedures for determining whether a waste contains contaminants in significant concentrations and whether a waste will release such contaminants under a variety of leaching conditions. Work on extended leaching is not planned as part of the project.

HAZARDOUS WASTE DECOMPOSITION

Waste Leachability

In lieu of the development of a Standard Leaching Technique, one current on-going hazardous waste leaching study (4) has been patterned after a method developed by the International Atomic Energy Agency (I.A.E.A.) for leach testing immobilized radioactive waste solids. Plexiglass columns of 0.35 cubic feet are loaded with the sample and a 1-inch head of leaching fluid is maintained on top of the samples. Two leaching fluids are used, deionized water and deionized water at a pH of 7.5 - 8.0. The two leaching fluids represent both sides of the pH scale since the deionized water will assume an acid pH due to its reaction with carbon dioxide. The selection of leaching fluids should provide some concept of the pH effect on leaching. Flow through the column is regulated to maintain a velocity of approximately 1×10^5 cm/sec, and leachate samples are collected at the base of the column. The columns are translucent and observations of flow patterns as well as possible biological activity can be made. Five industrial sludges and five Flue Gas Desulfurization (FGD) sludges are being investigated.

Another on-going leachability study (5) relates to the inorganic industrial waste where there is no appreciable biological activity. Consequently, the chief mode of decomposition and pollutant release is solubilization and other strictly chemical changes which take place as the waste is leached with water. Accordingly, the testing program is designed to evaluate leaching and pollutant release under a variety of leaching conditions which may be encountered in one or more disposal situations.

A major consideration in the leaching behavior of wastes is the pH. Consequently, three types of leaching tests similar to the one described above, are being utilized with leaching fluids at pH 5, 7, and 9 by mixing a sample of the waste with water and adding a mineral acid, as required to achieve the desired pH. The solution is then filtered and the contaminant concentration in the liquid phase is measured. A fourth type of leaching is conducted by mixing a sample of waste with deionized water and allowing the waste itself to control the pH; this type of leaching simulates the action of rainfall or other water while the pH-adjusted leachings simulate the effect of the co-disposal with strongly acid or alkaline wastes, or of disposal on soils of those pH's. A fifth type of leaching is conducted using municipal landfill leachate as the solvent. This highly odorous material contains many organic acids and is strongly buffered at a pH of about 5. Consequently, it has proved to be a very effective solvent. This type of leaching is carried out to simulate co-disposal of municipal and industrial wastes.

A second major consideration in the leaching behavior of wastes is time. Some wastes will not release appreciable amounts of contaminants until leaching has removed salinity or reserve alkalinity from the waste. Accordingly, each of the five types of leaching is extended over time. After the liquid has been in contact with the waste for 72 hours (agitated gently), the liquid is filtered off and a fresh volume of liquid is added. This process is repeated seven times, each time for a contact period of 72 hours. Results to date have indicated great variability in the time-dependent leaching behavior of wastes, confirming the need for careful consideration of this variable in managing land disposal.

Co-Disposal

Environmental effects from landfilling result from not only the soluble and slowly soluble materials placed in the landfill, but also the products of chemical and microbiological transformations. These transformations should be a consideration in management of a landfill to the extent that they can be predicted or influenced by disposal operations.

One current project (6) supporting development of the landfill design and operation manuals is a study of factors influencing (a) the rate of decomposition of solid waste in a sanitary landfill, (b) the quantity and quality of gases and leachate produced during decomposition, and (c) the effect of admixing industrial sludges and sewage sludge with municipal refuse. Seven industrial sludges and sewage sludge in three different amounts have been added to the simulated landfill test cells to evaluate the impact of a practice which, though opposed by EPA, is apparently prevalent in the United States as a method of disposal for hazardous wastes. Presently, little is known on what effect adding sludge has on the decomposition process, and quantity and quality of gases and leachate produced during decomposition. There is a strong concern that addition of sludges, particularly those high in trace and heavy metals, will result in elevated metal concentrations in the leachates and will pose a threat to potable groundwater supplies. Advocates of co-disposal of sludges with municipal waste believe that presence of organics in the landfill will immobilize trace and heavy metals and, further, that the presence of such sludges may accelerate the decomposition process and shorten the time required for biological stabilization of the refuse. Periodic analysis of the leachates in this study for trace and heavy metals is expected to provide answers to some of these questions and to allow rational evaluation of the practice of co-disposal.

Poliovirus (6) was also added to one of the simulated landfill cells and the leachates from all cells are being assayed for fecal coliform and fecal streptococci to study the potential health impacts of landfilling. It has been assumed that the environment within a landfill is generally antagonistic to pathogenic organisms, and poliovirus has been shown in vitro to have a very low survival in landfill leachates. However, other studies have demonstrated the presence of poliovirus in leachate when municipal solid waste has been leached rapidly, and fecal streptococci have been found over long periods of time in landfill leachates. Fecal coliforms were also present, but their numbers in leachate decreased considerably within several months after placement of refuse.

POLLUTANT MIGRATION THROUGH SOILS

Present management of land disposal of hazardous wastes is frequently inadequate. Significant environmental impacts from such activities are not mere possibilities--actual damages to groundwater have occurred and are well documented. Although the potential for damage in general can be demonstrated, migration patterns of contaminants and consequent damages which would result from unrestricted landfilling at specific sites cannot be predicted accurately. The ability to do this must be developed in order to justify the requirement for changes in the design and operation of disposal sites, particularly for any restriction of co-disposal. Consequently, a significant number of the research projects funded by SHWRD are focused on understanding the process and predicting the extent of migration of contaminants (chiefly heavy metals) from land disposal sites for municipal and hazardous wastes. This research is:

--studying migration of hazardous materials in soils,
--documenting movement of such materials to establish the link

to health/environmental effects,
--establishing role of soil in controlling or reducing the amount of harmful substances reaching water or air.

These pollutant migration studies are being performed simultaneously in the areas of (a) industrial hazardous wastes, (b) municipal refuse, and (c) specialized wastes. Several previous reviews* of these efforts have been presented.

Bibliography and State-of-the-Art

The initial effort (5) in this area resulted in a bibliography relating to the disposal of hazardous wastes, other than sewage sludge, on land. It comprises the results of a search of recent literature and includes information on the transport, transformation, and soil retention of arsenic, asbestos, beryllium, cadmium, chromium, copper, cyanide, lead, mercury, selenium, zinc, halogenated hydrocarbons, pesticides, and other hazardous substances. In order to limit the size of the resulting publication, the literature search focused on processes directly related to transport (adsorption, ion exchange, etc.) and documentation of the occurrence and extent of transport while specifically excluding topics such as uptake and translocation by plants, theoretical modeling, and effects on microorganisms and processes mediated by microorganisms. The bibliography has been divided into two volumes to facilitate its use; the pesticides citations have been placed in a separate volume and detailed information on chemical nomenclature and structures of pesticides appended to this volume.

The second effort (5) relates to a "state-of-the-art" document on migration through soil of potentially hazardous pollutants contained in leachates from waste materials. The document presents a critical review of the literature pertinent to biological chemical, and physical reactions, and mechanisms of attenuation (decrease in the maximum concentration for some fixed time as distance traveled) of selected elements such as arsenic, beryllium, cadmium, chromium, copper, iron, mercury, lead, selenium, and zinc, along with asbestos and cyanide in soil systems.

Controlled Lab Studies

This initial effort (5) is examining the factors which attenuate contaminants (limit contaminant transport) in leachate from municipal solid waste landfills. Although the work is strongly oriented toward problems with disposal of strictly municipal wastes, the impact of co-disposal of municipal and hazardous wastes is also considered. The project is concerned with contaminants normally present in leachates from municipal solid waste landfills and with contaminants that are introduced or increased in concentration by co-disposal of hazardous wastes. These contaminants are: arsenic, beryllium, cadmium, chromium, copper, cyanide, iron, mercury, lead, nickel, selenium, vanadium, and zinc.

The general approach was to pass municipal leachate as a leaching fluid through columns of well characterized, whole soils, containing a variety of organic and inorganic substances, maintained in a saturated, anaerobic state. The leaching fluid consisted of typical municipal refuse leachate with high concentrations of metal salts added to achieve a nominal concentration of 100 mg/l. The most significant factors were then inferred from correlation of observed migration rates and known soil and contaminant characteristics. This effort will contribute to the development of a computer simulation model for predicting trace element attenuation in soils.

The second effort (5) in this area is studying the removal of contaminants from landfill leachates by soil clay minerals. Soil columns were utilized and packed with mixtures of quartz sand and nearly pure clay minerals. The leaching fluid consisted of "as is" typical municipal refuse leachate without metal salt additives. The general approach to this effort was similar to that described in the preceding effort except that (1) both sterilized and unsterilized leachates were utilized to examine the effect of microbial activity on hydraulic conductivity, and (2) extensive studies of the sorption of contaminants from leachate on the clay minerals as a function of pH and the composition of leachate were investigated.

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*Roulier, M. H. Research on Minimizing Environmental Impact from Landfilling; Research on Contaminant Movement in Soils. Presented at a meeting of the NATO Committee for Challenges to Modern Society, Project Landfill. Oct. 20-23, 1975, London, England.

The third effort (5) is examining the potential for contaminant migration from industrial hazardous wastes disposed of on land. After the composition and leachability of a waste has been established, a leachate from the waste is applied to columns of various soils in the laboratory to allow study of rates of movement of contaminants. Wastes are being studied or are scheduled for study from the following industries:

Electroplating
Inorganic pigments
Water-based paints
Nickel-cadmium batteries
Chlorine
Lead-acid batteries
Carbon-zinc primary batteries
Hydrofluoric acid
Phosphorous
Aluminum fluoride
Titanium pigments
Re-refining of used petroleum
Flue Gas Desulfurization (FGD)

Because of the chemical complexity of hazardous wastes, it is not possible to simulate them; actual wastes are being collected and used in the project. Many of these wastes are being disposed of with municipal wastes. To assess the potential adverse effects of co-disposal, the industrial wastes are leached with municipal landfill leachate as well as water. Results to date indicate that when compared with water, municipal landfill leachate solubilizes greater amounts of metals from the wastes and promotes more rapid migration of metals through soil. The soils being used in this study are similar to those being investigated by the above described activities. It is anticipated that during the life of this effort, studies will be conducted on 43 industrial wastes, 3 types of coal flyash, and 6 sludges generated by the removal of sulfur oxides from the flue gases of coal-burning power plants.

The fourth effort (5) is a laboratory study of the migration and degradation in soil of the pesticides Methyl Parathion, 2,4-D, Atrazine, Trifluralin, and Terbacil applied at concentrations much higher than those used in normal agricultural practice. The intent of the project is to supply information applicable to problems encountered in land disposal of pesticides and solutions from the washing of pesticide application equipment. Such information is presently lacking because most work to date has been conducted from an agricultural rather than a disposal point of view and very low application rates have been used. The project includes work on adsorption-desorption, chemical-microbial degradation, production of metabolites, and soil column studies of migration rates. Data collected during the study will also be used to test the applicability (at high concentrations) of existing pesticide migration models in predicting the rate and extent of movement through soil. Work on this project has only recently been initiated and no results are available.

Field Verification

The initial effort (5) is to test current assumptions about the effectiveness of clays and other fine textured earth materials in restricting the movement of contaminants into groundwaters. This work is examining patterns of contaminant migration around two secondary zinc smelting plants and an organic chemical manufacturing plant that are storing or disposing of their wastes on land. The soils in the area are quite fine textured and, based on current knowledge of contaminant migration, should provide safe disposal sites.

The second effort (5) relates to the use of simulation modeling as one method of predicting contaminant movement at disposal sites. The two-dimensional model which was used successfully to study a chromium contamination problem is being developed into a three-dimensional model and will be tested on a well-monitored landfill where contaminant movement has already taken place. Although this type of model presently needs a substantial amount of input data, it appears promising for determining contaminant transport properties of field soils and, eventually, predicting contaminant movement using a limited amount of data.

Organic Contaminants

A planned effort (2) to be initiated this fiscal year relates to organic contaminant attenuation by soil. Much more is known about wastes containing inorganic contaminants than those containing organic contaminants. Analytical techniques for inorganic materials are well developed and relatively cheap compared to analytical techniques for organic materials which are both time consuming and expensive. The problem is compounded by the fact that organic contaminants are more numerous and more are being synthesized all the time.

Work on predictive techniques has been included as a part of all contaminant migration projects because the results from this type of work are only useful insofar as they can be applied to situations which have not been studied. The results to date lack generality and no one predictive technique can be advocated at this time.

CONTROL TECHNOLOGY

Control technology is needed because experience and case studies have shown that some soils will not protect groundwater from contaminants. Even in "good soil," selected sites may have to be supplemented by additional protection to prevent subsurface pollution from especially hazardous wastes. To minimize the impact of placing hazardous wastes in conventional landfills, treatments under investigation are directed either at modification of the waste prior to disposal or modification of the waste disposal site.

Treatments

Natural Soil Processes:

The treatment of pollutants (5) from hazardous waste and municipal refuse disposal sites by natural soil processes is basically being performed under the "Pollutant Migration Through Soils" studies whereby various raw soils are being evaluated in column studies for their pollutant attenuation capabilities. The U.S. Department of Agriculture (USDA) soils series currently being investigated are: Anthony, Ava, Chalmers, Davidson, Fanno, Kalkaska, Mohave, Molokai, Nicholson, and Wagram. These soils encompass the range of soil types--from sand to clays to silts. Other soils are also being investigated whereby various percentages of the clay mineral, kaolinite, montmorillonite, and illite are mixed with pure sand to form various mixtures of sand and clay soils.

Physical/Chemical/Biological:

Recognizing the present inadequacy of treatment/disposal technology for hazardous materials, a SHWRD in-house research project (4) was initiated that resulted in a report describing promising methods for treating complex waste streams and provide resource recovery potential. These promising methods identified were:

Chlorinalysis
Wet air oxidation
Decomposition by acids and bases
Chemical oxidation
Other chemical treatments
Biological degradation
--enzymes
--trickling filters
--activated sludge
Catalysis
Batch and continuous ion exchange
Photochemical processing
Low-temperature microwave discharge
Osmosis/ultrafiltration
Activated carbon absorption

Another in-house study (7) was conducted to determine the impact of hazardous materials released into the environment. This study revealed that many of the materials discharged are persistent or nonbiodegradable, will bioaccumulate in man, and pose a serious threat to all living systems.

A number of research efforts have been initiated to develop and evaluate promising treatment techniques, previously identified, for control of hazardous materials. The initial effort (7) relates to the chlorinalysis process which appears to be a very desirable process for eliminating some very toxic and hard to dispose of chlorocarbons and pesticide residues. This was a technical and economic study of the feasibility of converted highly toxic wastes to carbon tetrachloride and other useful chemicals. Laboratory studies have confirmed that herbicide orange, still bottoms from organic manufacturing operations, and pesticides all can be converted to the principal useful chemical, carbon tetrachloride.

A second effort (4) relates to the investigation of catalytic techniques for decomposing pesticides and other toxic wastes to safe, reusable by-products. Basically, the catalytic hydrogenation of chlorinated organic compounds is being studied. While the results of catalysis are not as favorable as those of chlorinalysis, there is evidence that a catalyst may be discovered that will remove the group of elements conferring toxicity to a parent structure, and thereby provide a feedstock for the synthesis of new useful chemicals.

A third effort (7) relates to the assessment of techniques for the detoxification of selected hazardous materials. The existing techniques previously identified, including hydrogenation, are being assessed for efficacy and practicality. This also includes chemical and toxicological investigation of all products and residues provided in the above discussed incineration or developing detoxification studies.

A fourth effort (5) relates to a laboratory evaluation of ten natural and synthetic materials (bottom ash, flyash, vermiculite, illite, Ottowa Sand, activated carbon, kaolinite, natural zeolites, activated alumina, cullite) for the removal of contaminants in the leachate and liquid portion of three different industrial sludges (calcium fluoride sludge, petroleum sludge, metal finishing sludge). This investigation involves beaker studies to evaluate the static adsorption capacity of sorbent materials using maximum background concentrations of contaminants in the leachate, followed by lysimeter studies to obtain information regarding the dynamic absorption capacity and permeability characteristics of these materials. The analysis of the leachate involves the determination of pH, conductivity, residue, chemical oxygen demand (COD), total organic carbon (TOC), anionic species, and cationic species before and after contact with sorbent materials.

Thermal Decomposition:

Treatment by thermal decomposition relates to the establishment of time-temperature relationships for incinerating pesticides. Specifically, through the test program, existing information will be summarized into a state-of-the-art document and experimental incineration/decomposition studies will be conducted on approximately 40 pesticides. A lab scale evaluation/confirmation study and a pilot scale incinerator study are being performed. The pesticides investigated for thermal decomposition were:

DDT	Toxaphene
Aldrin	Captan
Picloram	Zineb
Malathion	Atrazine

The initial effort (2) relates to the determination of incineration conditions necessary for safe disposal of pesticides. An experimental incinerator was constructed and utilized to determine the time-temperature conditions needed for the safe destruction of pesticides. This research is being supplemented by another effort documenting in detail the various research projects relating to thermal destruction of pesticides. Efficiencies of combustion, residence time, and other parameters for safe incineration were documented.

A second effort (2) relates to the development of laboratory scale methods for determining the time-temperature relationships for the decomposition of pesticides. The successful achievement of this effort would allow the use of quick laboratory test methods to determine best incineration conditions for full-scale destruction of pesticides.

Isolation

Underground Cavities:

The isolation technology for underground cavities offers attractive disposal sites for very concentrated toxic hazardous wastes. Efforts have been performed to evaluate the adequacy of:

--deep-well injection (for liquid waste disposal) including wells and permeable formations

--salt mines and hard-rock mines for storage of solid, fixed, or encapsulated wastes

The first effort (8) consisted of a review and analysis of available information related to deep-well injection, and an assessment as to the adequacy of this method for managing hazardous wastes and ensuring protection of the environment has been made. The study provided a comprehensive compilation of available information regarding the injection of industrial hazardous waste into deep wells. Limited assessments made indicated that deep-well injection of selected wastes is environmentally safe provided sound engineering and geologic practices are followed in constructing the well and in operating the well. Geologic and engineering data are available in many areas to locate, design, and operate a deep-well system for injecting hazardous liquid wastes into saline aquifers (Salaquifers) and other deep strata. However, there is a paucity of information on salaquifer chemistry and the chemical and microbiological reactions of wastes within a receiving salaquifer. Federal and state statutes and regulations vary greatly or are nonexistent to answer problems arising from the use of interstate or intrastate aquifers. Regardless of these identified problems, deep-well injection remains a viable alternative for waste management.

The second effort (8) consisted of a review and analysis of information on the placement of hazardous waste in mine openings. The study assessed the technical feasibility of storing nonradioactive hazardous wastes in underground mine openings. The results showed that a majority of the wastes considered can be stored underground in an environmentally acceptable manner if they are properly treated and containerized. Various mine environments in the United States are applicable for such storage, room and pillar mines in salt, potash, and gypsum appear to be the most favorable. This review concluded that storage in underground mines is an environmentally acceptable method of managing hazardous wastes provided the recommended procedures of site selection, treatment, containerization, and waste handling are followed. The study showed that there now exists within the United States environmentally suitable underground space for the storage/disposal of hazardous wastes. Systems adequate to detect, monitor, and control waste migration are available or can be developed from current technology.

Encapsulation:

The encapsulation technology program is evaluating promising organic and inorganic processes for both fixing and coating hazardous materials of pesticides, soluble organics, and heavy oily residues. The process relates to fixing the material in a 55-gallon drum or up to a 500-pound block and then encapsulating the drum or block with a nonporous plastic coating.

The initial effort (8) relates to organic process to effectively encapsulate hard to manage hazardous waste into a relatively dense mass which will not pollute and could be utilized or disposed in roadbeds, mines, or fill areas.

Stabilization

Stabilization is achieved by incorporating the solid and liquid phases of the waste into a relatively inert matrix which is responsible for increased physical strength and which protects the components of the waste from dissolution by rainfall or by soil water. If this slows the rate of release of pollutants from the waste sufficiently so that no serious stresses are exerted on the environment around the disposal site, then the wastes have been rendered essentially harmless and restrictions on where the disposal site may be located will be minimal.

Chemical Fixation:

The initial chemical fixation effort (4) relates to the transforming of the waste into an insoluble or very low solubility form to minimize leaching. The test program consists of investigating five industrial waste streams, both in the raw and fixed state. Each waste stream will be treated with five separate fixation processes and subjected to leaching and physical testing. These lab studies will identify which processes should be evaluated in the field by using large scale field plots or lysimeters. Co-disposal of the fixed waste with municipal refuse will also be investigated. The five industrial wastes being investigated are the same as those being researched under the pollutant migration study:

electroplating
chlorine production
nickel-cadmium battery production
inorganic pigment manufacturing
calcium fluoride (electronics)

The following fixation processes will be utilized with either industrial waste or flue gas desulfurization waste (SO_x). The assignment of processors to sludge categories is shown below:

Processor	Sludge Category Industrial Waste	Flue Gas Desulfurization
1. International Utilities Conversion System, Inc. (IUCS)	X	X
2. Chem-Fix, Division of Environmental Sciences	X	X
3. Nuclear Engineering Company -- Tiger-Lok Process	X	
4. Wehran Engineering -- Krete-Rok Process		X
5. TRW Systems Group, Inc. -- Organic Binder	X	
6. Lancy Lab		X
7. Dravo	Calcium fluoride only	X

The second effort (4) will identify additional stabilization processes that have potential application to landfilling of hazardous wastes, study the chemistry of these processes to eliminate duplication of work already underway, and then evaluate selected processes using the procedures already developed.

The third effort (4) is a series of field verification studies to assess the success with which pollutants have been immobilized at landfills receiving stabilized hazardous and SO_x wastes. Detailed subsurface investigations will identify any pollutant movement away from such sites and interactions with soils that have accelerated or retarded such movement. Sites will be selected to give the widest possible range of stabilization processes, wastes, and soils.

Liners/Membranes:

The liner/membrane technology is being studied to evaluate suitability for eliminating or reducing leachate from landfill sites of industrial hazardous wastes and SO_x sludge wastes. The test program will evaluate in a landfill environment, the chemical resistance and durability of the liner materials over a 12- and 24-month exposure period to leachates derived from industrial wastes, SO_x wastes, and municipal solid wastes. Acidic, basic, and neutral solutions will be utilized to generate industrial waste leachates.

- Hazardous Waste Liners--The initial effort (4) relates to the investigation of materials for use as liners for hazardous waste disposal sites that will be tested in rectangular, epoxy-coated steel cells (25 cm by 38 cm) containing about 30 cm of the hazardous waste above the material being tested. Since the composition of the leachate from hazardous wastes is determined mainly by the solubility products of the components and is not expected to change significantly over the period of the experiment, no provision has been included for drawing leachate from above the liner material. Any leachate passing through the liner will be collected and analyzed to determine whether there is selective passage of hazardous substances from the waste. A number of materials are under consideration for study as primary liner materials. Final selection will be made from the following list:

Polymeric membranes

Butyl rubber
Chlorinated polyethylene (CPE)
Chlorosulfonated polyethylene (Hypalon)
Ethylene propylene rubber (EPDM)
Neopreme
Polyvinyl chloride (PVC)
3110 (a PVC-type material by DuPont)

Admixed materials

Bentonite clay seal
Emulsified asphalt (Petromat)

Soil cement
Hydraulic asphalt concrete
Compacted fine grained soil
Polymeric bentonite sealant
Acid-resistant concrete
Hot sulfur

A second effort (5) relates to a laboratory evaluation of various materials which could be utilized as retardant materials to minimize migration of pollutant from disposal sites. This investigation will study the following materials on a pilot plant basis: (a) agricultural limestone, (b) hydrous oxides of Fe (ferrous sulfate mine waste), (c) lime-sulfur oxide (stack-gas waste), (d) certain organic wastes, and (e) soil sealants. Preliminary research on limestone and Fe hydrous oxide liners indicates these materials have a marked retarding influence on many of the trace elements.

- SO_x Sludge Liners--The initial effort (4) relates to the types of materials to be tested for use as liners for sites receiving sludges generated by the removal of sulfur oxides (SO_x) from flue gases of coal-burning power plants which will be somewhat different from those used in the municipal and the hazardous waste studies. The volumes of SO_x sludge generated in any particular place will, typically, be much greater than those for other types of wastes, the disposal sites will be large, and the hazards (leachable trace and heavy metals) associated with the sludge will not be great. Consequently, methods of lining such disposal sites must have a low unit cost to be covered. It is desirable that the materials be easy to apply. Because of these considerations, the number of polymeric membranes included in the study have been reduced whereas admixed and sprayed-on materials are being emphasized. A total of 18 materials/processes will be selected from the following:

Polymeric

Polyvinyl chloride
Polyethylene

Admixed

Soil cements
Lime stabilized soils
Asphalt cements
Emulsion asphalts
Chemically stabilized SO_x sludge

Sprayed-on

DCA 1295
Uniroyal
Dynatech
Plastics
Asphalts
Hot sulfur

SPECIALIZED WASTES

The specialized waste test program relates to hexachlorobenzene, vinyl chloride monomer, (VCM), and oil spill debris.

--Hexachlorobenzene (HCB) wastes are being investigated to determine the volatilization aspects of the material and to evaluate the effectiveness of various materials for covering these wastes to reduce volatilization.

--Vinyl Chloride Monomer (VCM) is retained in polyvinyl chloride (PVC) processing sludge wastes. These sludges are being investigated to determine the amount of VCM present and the volatilization aspects of the material.

--Oil Spill Debris disposal from cleanup efforts is being investigated to determine the best practicable technical options available for disposal.

Hexachlorobenzene (HCB)

The initial effort (5) relates to an evaluation of the effectiveness of the procedures presently being used to seal HCB landfills by measuring the rate of movement of HCB through soil, water, and polyethylene film. Results of the study, being conducted under contract, will be used to specify the conditions, if any, under which is safe to store or dispose of HCB-containing wastes on land. The general approach is to measure the steady state vapor flux of HCB under laboratory conditions and then, using Fick's first law, to calculate the diffusion coefficient for HCB in that material. Once the diffusion coefficient is known, the flux through other thicknesses of the material can be calculated.

Planned future work on this effort will examine the effect of soil water content on the HCB diffusion coefficient and predicted fluxes through soil and will use another HCB-containing waste to verify the assumption that HCB flux is not affected by other substances present in the wastes (e.g., hexachlorobutadiene, pentachlorobenzene).

Vinyl Chloride Monomer (VCM)

The initial effort (9) relates to a low level study done to determine whether a potential threat to the health of landfill workers or nearby residents exists. Seventeen grab air samples were collected for laboratory analysis of VCM content at three landfills where these sludges were disposed. Samples of the PVC sludges which were disposed at the three landfills also were collected. VCM concentrations in the grab air and sludge samples were measured using the gas chromatographic-flame ionization detection analytical technique. The release rate of VCM from sludge also was measured under controlled laboratory conditions, using a specially designed apparatus. The VCM emissions potential of the total sludge quantities disposed at these landfills was calculated.

Oil Spill Debris

The initial effort (10) is being performed by the Industrial Environmental Research Laboratory (IERL) of EPA, OR&D, and relates to the development of a detailed, practical how-to-do-it manual for oil spill debris disposal and to the making of an accompanying film for State and local officials. A literature search has been carried out, sites for confirming field studies chosen, and some film footage taken. Present recommendations for disposal of unrecyclable material include individual burial, incorporation into an approved sanitary landfill, and land spreading.

ALTERNATIVES FOR HAZARDOUS WASTE LANDFILLS

Land Cultivation

The disposal technique of land cultivation, whereby specific waste residues have been directly applied or admixed into soils, has been an alternate disposal option for many years for oily waste materials. Since many industrial waste sludges have similar characteristics to oily waste materials, it appears that land cultivation could be viable alternative to landfilling of hazardous industrial sludges. Consequently, a planned research effort (4) this fiscal year will prepare a state-of-the-art document to assess and determine the feasibility and beneficial aspects of land cultivation of hazardous industrial sludges including oily waste materials. This state-of-the-art effort would then be followed by technical and economic assessment effort.

CONCLUSION

The laboratory and field research project efforts discussed here reflect the SHWRD overall effort in hazardous waste management research. The projects will be discussed in much more detail by the following speakers. More information about a specific project or study can be obtained by contacting the project officer whose name, address, and phone number is listed in this paper. Inquiries can also be directed to the Director, Solid and Hazardous Waste Research Division, Municipal Environmental Research Laboratory, U.S. Environmental Protection Agency, 26 West St. Clair Street, Cincinnati, Ohio 45268. Information will be provided with the understanding that it is from research in progress and conclusions may change as techniques are improved and more complete data become available.

EPA PROJECT OFFICERS

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OSWMP CHEMICAL WASTE LANDFILL AND RELATED PROJECTS

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ABSTRACT

The Office of Solid Waste Management Programs conducts a variety of studies and demonstrations designed to provide data base and support for the formulation of guidelines for the treatment and disposal of hazardous wastes. These projects take the form of studies, analyses, field investigations, and demonstrations. A major undertaking presently being planned is a study of management options for predicting pollution potential from waste disposal on land. In another area, the Office's largest single hazardous waste project, the Chemical Waste Landfill Demonstration is currently getting underway in Minnesota. This paper discusses the technological and scientific aspects of these two projects. In addition, tables at the end summarize other OSWMP hazardous waste projects and list Office reports.

BACKGROUND

Until relatively recently, comparatively little attention has been given to the disposal of hazardous wastes. However, as air and water pollution regulations are implemented, quantities of industrial sludges, slurries, and liquids, some of which are toxic or otherwise hazardous, are increasing rapidly. The Office of Solid Waste Management Programs (OSWMP) urges that the following priorities be considered in managing hazardous wastes:

(1) Recycling,

(2) Material Recovery,

(3) Energy Recovery,

(4) Physically/chemically/or biologically treat the waste to permit recycling or recovery,

(5) Incineration,

(6) Treat the waste so as to detoxify it,

(7) Treat the waste so as to immobilize the hazardous materials or reduce volume.

(8) Land Disposal

There are a number of processes, techniques, and equipment designs available for managing wastes in this manner, but by and large, wastes have been and continue to be disposed of in a least-cost manner for the producer/disposer of the wastes. These least-cost disposal methods are often inadequate to protect the environment and the public health. The methods of treatment and disposal which are most often used are landfilling, incineration, and dumping in pits or lagoons. Land disposal, due to its relative economy, is the method preferred by disposers and will likely remain as such unless regulatory action precludes this approach. Numerous case histories attest to groundwater pollution as a result of land disposal of hazardous and other wastes.[1]

In view of the preference that has been shown for land disposal, OSWMP is undertaking several projects to investigate the adequacy of land disposal technology for potentially hazardous wastes.

STANDARD ATTENUATION PROCEDURE

It is clear that although a waste may contain one or more hazardous substances; whether they pose a groundwater pollution threat will depend on a variety of factors including: quantity of waste, leachability, rainfall, permeability, and attenuative properties of the soil, and distance to and quality of the groundwater. In most cases, it is not known beforehand whether these site and waste characteristics will result in pollution. In fact, due to limited or non-existing monitoring, pollution incidents are not usually predicted or known until actual damage has been experienced. To protect the public health and the environment it is desirable to develop a procedure or procedures at any given site which can (1) evaluate the potential for groundwater degradation from potentially hazardous wastes, or (2) determine whether a harmful (polluting) quantity of waste is involved in a given waste disposal situation. Ideally, such a technique could also be used to determine the maximum safe loading of any waste on or in any given land parcel. Probably maximum utility can be realized by use of the technique as a standard tool in the site permit decision making process by regulatory agencies. As such, it would provide a uniform, organized approach to decision making based on site/waste specific data.

Accordingly, OSWMP is embarking upon a program which may lead to development of a decision making tool, capable of predicting groundwater pollution potential based on the characteristics of the disposal site and the wastes to be disposed. At the present time it is not clear which of several possible approaches to development of such a procedure is optimum. That is, should it include a model, a decision tree, criteria ranking process, or other methods? It is also not clear to what extent various techniques have been developed or perhaps, are in use.

Therefore, as a first step, OSWMP will determine the state of the development and evaluate the potential usefulness of techniques for predicting groundwater pollution potential from disposal of specific wastes on specific land parcels.

Objectives are as follows:

1. determine what viable techniques are in use or under development.
2. assess the potential of possible techniques or approaches (in use or proposed) for development of a standard procedure,
3. estimate the costs, work and time requirements for development of a working standard procedure for each viable option, and
4. prepare in detail, a developmental program for the technique or combination of techniques judged to be the best.

The study work period will be nine months with a final report being published in about one and one-half (1 1/2) years.

CHEMICAL WASTE LANDFILL DEMONSTRATION

In addition to developing a tool to assist in evaluating pollution potential, OSWMP is deeply involved in identifying and demonstrating alternatives to improper disposal. One of the alternatives is to have a regional chemical waste disposal facility, privately operated but government owned where the local government provides facilities for proper disposal and, through regulation and strict enforcement, prevents improper disposal within the region. OSWMP is sponsoring a demonstration of this approach with a grant to the Minnesota Pollution Control Agency to build and operate a chemical waste landfill. The objectives of this grant are to demonstrate:

. how local governments can organize and finance such a venture

. regulation and enforcement necessary to make it work

. arrangements for long-term care of the site

. public involvement in hazardous waste disposal, and existing technology.

Development of information on technologies is of limited value if that information is not interpreted and disseminated. Furthermore, technology alone will have limited impact if other important issues such as planning, financing, procuring and managing are not addressed as well. Demonstrations supported by OSWMP, which install technology into operating solid waste management systems, develop the information needed to assist communities in decision making. These projects must consider whether the technologies under demonstration are economically viable and can be transferred to "real-world" situations. They must be designed to consider not only the technological efficacy, but how systems can be adopted by political decision makers.

An important technological consideration in the concept of this project is to make land disposal sites suitable for the receipt of hazardous wastes by carefully choosing the best site available and by designing the facility so as to overcome the shortcomings of the site. Proper design when coupled with sound management techniques will also prevent accidents, fires and explosions, air pollution incidents and other mishaps which are common in many land disposal sites today.

In dry areas of our country, land disposal can usually be carried out in a sound and safe manner using well managed solar evaporation, soil incorporation, and trench disposal techniques. However, a majority of the industrial waste (estimated at 65 percent) is generated in the humid regions, mostly east of the Mississippi River.[2] Humid regions are characterized by annual precipitation rates that are in excess of annual evapotranspiration rates, thus creating a potential leachate management problem.

Technology concepts for land disposal of chemical wastes in humid regions have been developed but never demonstrated on a commercial scale. Commercial-scale demonstration of the environmental adequacy, economic feasibility, and operating practicability of a variety of currently promoted land disposal concepts is needed before workable disposal guidelines and regulations can be developed.

The technological and scientific aspects of the project include:

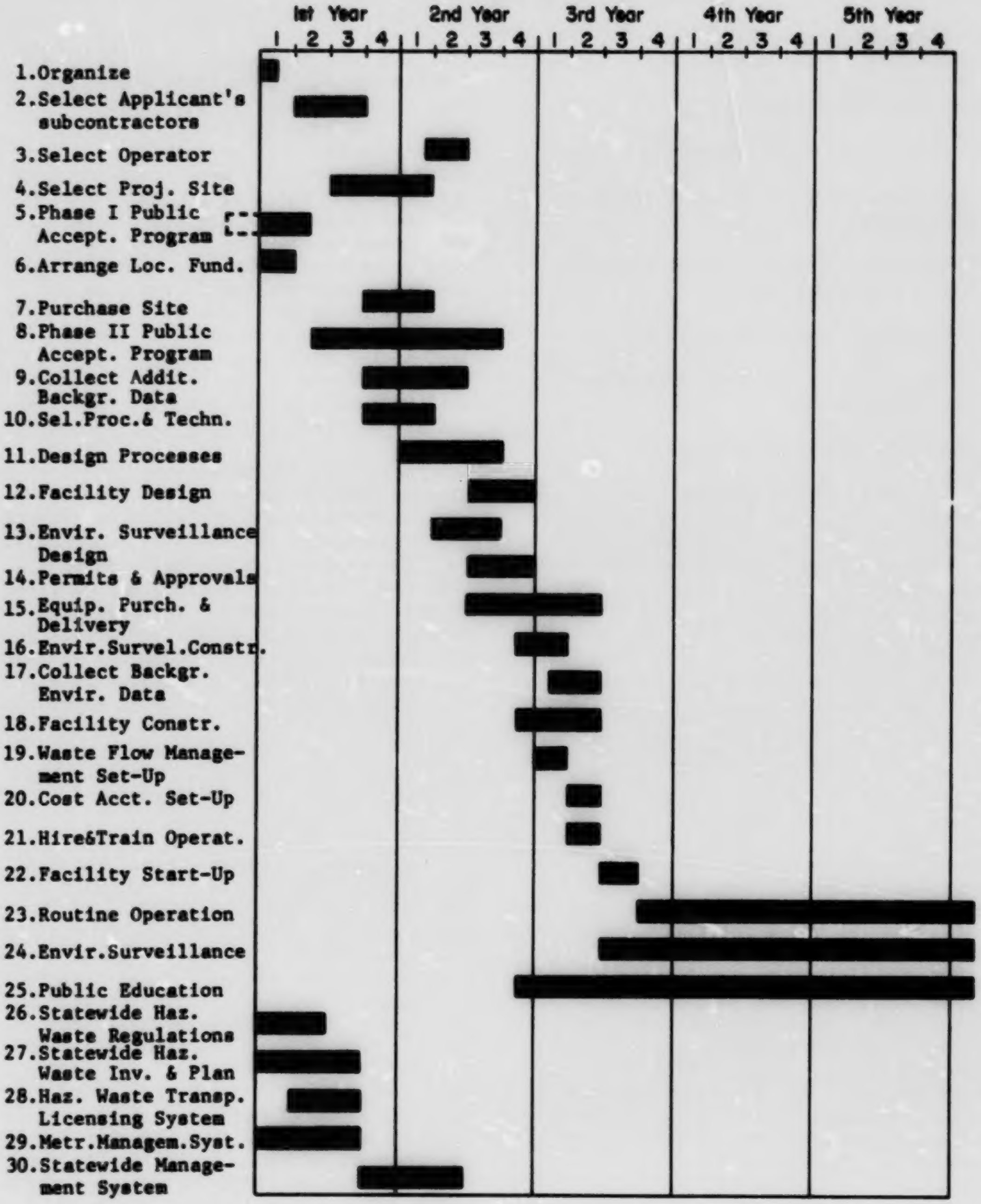
- demonstration of site selection methods
- demonstration of appropriate site preparation techniques to prevent groundwater infiltration
- demonstration of monitoring and surveillance techniques
- evaluation of waste handling and operational procedures
- determination of costs
- evaluation of social and institutional issues

The proposal submitted by the Minnesota Pollution Control Agency (PCA) ranked highest among eight finalists who submitted formal applications and was selected for the grant award.[3]

The grant period is for five years with a total cost of $5.4 million dollars, three-quarters ($3.72 million) of which will be funded by the federal government and one quarter ($1.69 million) funded by local sources. The project's implementation is scheduled as follows: the first 2 1/2 years will be directed to planning, design, and construction of the facility; the landfill will open in late 1977 and operate as a demonstration project until mid-1980 (Figure 1). It will continue to serve the region's chemical waste disposal needs after the demonstration period ends in 1980.

The PCA has contracted with the Metropolitan Waste Control Commission (MWCC), a State chartered regional operating authority, to implement planning, and construction of the facility as the managing agency. The MPCA will oversee the project, manage public education and citizen acceptance aspects of the project, and eliminate improper disposal through regulation and enforcement. Design and environmental assessment activities will be performed by consultants under contract to the MWCC. Similarly, actual day-to-day operation will be contracted to a private firm.

Figure 1. Demonstration Period



For purposes of discussion in this paper, the demonstration program may be considered in two parts: proposed sites and technical design and waste handling procedures.

Proposed Sites. The site selection criteria used by the grantee emphasized:

- low population density
- compatibility with adjacent land uses
- close proximity to chemical waste generators
- homogeneous soil well above recorded high groundwater levels
- groundwater discharge areas
- adequate water and power supply with good site access
- low flora and fauna diversity

Six sites in the greater Minneapolis/St. Paul metropolitan area were identified and subjected to further analysis during the proposed stage. Additional site evaluation studies are planned. As of now, of the sites investigated, the Flying Cloud site, a 36-hectare (90-acre) parcel in Hennepin County, is the site that best satisfies the selection criteria and is considered to have the greatest potential for this demonstration as of this time. The Flying Cloud site is located immediately north of the Minnesota River in Eden Prairie Township in the southwest portion of the metropolitan Minneapolis/St. Paul area. It is adjacent to the Flying Cloud Airport on the north and east and is accessible by way of U.S. Highway 169-212 (Figure 2). The site is 26 kilometers (16 miles) from the major industrial center of the region.

Existing land use is quasi-public and private with open fields and idle cropland. Low fauna and flora diversity is typical of such land use, pioneer species of vegetation and small animals are most predominant. Ultimate land use in the vicinity of the site will be for industrial purposes (Figure 3).

The area is not densely populated. Peak density during working hours is approximately 125 people per square mile. Projected and planned population densities for the City of Eden Prairie will not be reached until after the facility has been closed and such residential development will not be permitted in the vicinity of the demonstration facility.

The site is located on a bluff overlooking the Minnesota River Valley and well above (50 meters) the river's floodplain. The property boundary extends all the way to the river and, thus includes the river embankment and floodplain immediately below the bluff. The river embankment and floodplain have been designated as open space by the City of Eden Prairie and will be maintained as open space by the grantee. Construction of the proposed facility would be on the bluff, well back from the river embankment. A series of land-locked surface depressions or glacial kettles (Figure 4) can be used to control surface runoff and help assure that the quality of surface waters is maintained.

Approximately 50 meters (159 feet) of glacial outwash and grey till deposits overlie Prairie-du-Chien dolomite (Figure 5). Groundwater in this area, the Prairie-du-Chien aquifer, is typically 50 meters (150 feet) below the surface and discharges to the Minnesota River. The discharge rate has been estimated to be 1,170 liters (310) gallons per minute. Although the aquifer is a source of drinking for residents of the metropolitan area, drinking water wells and supply points are located upgradient (north) of the proposed site. The quality of the groundwater beneath the site would be maintained by an environmental fail-safe design.

Technical Design and Waste Handling Procedures. The geographic location of the project and the permeability of the overburden indicate that leachate migration and groundwater infiltration from the landfill would occur if not for the addition of impermeable barriers (liners) and leachate collection systems below each burial area. Therefore, such precautions will be absolutely necessary if the project's objective to demonstrate land disposal of chemical wastes so as to preclude leachate migration and groundwater quality degradation, is to be achieved. To this end, the Minnesota PCA has proposed three levels of environmental safeguards to manage chemical waste leachate. The primary level of protection will consist of

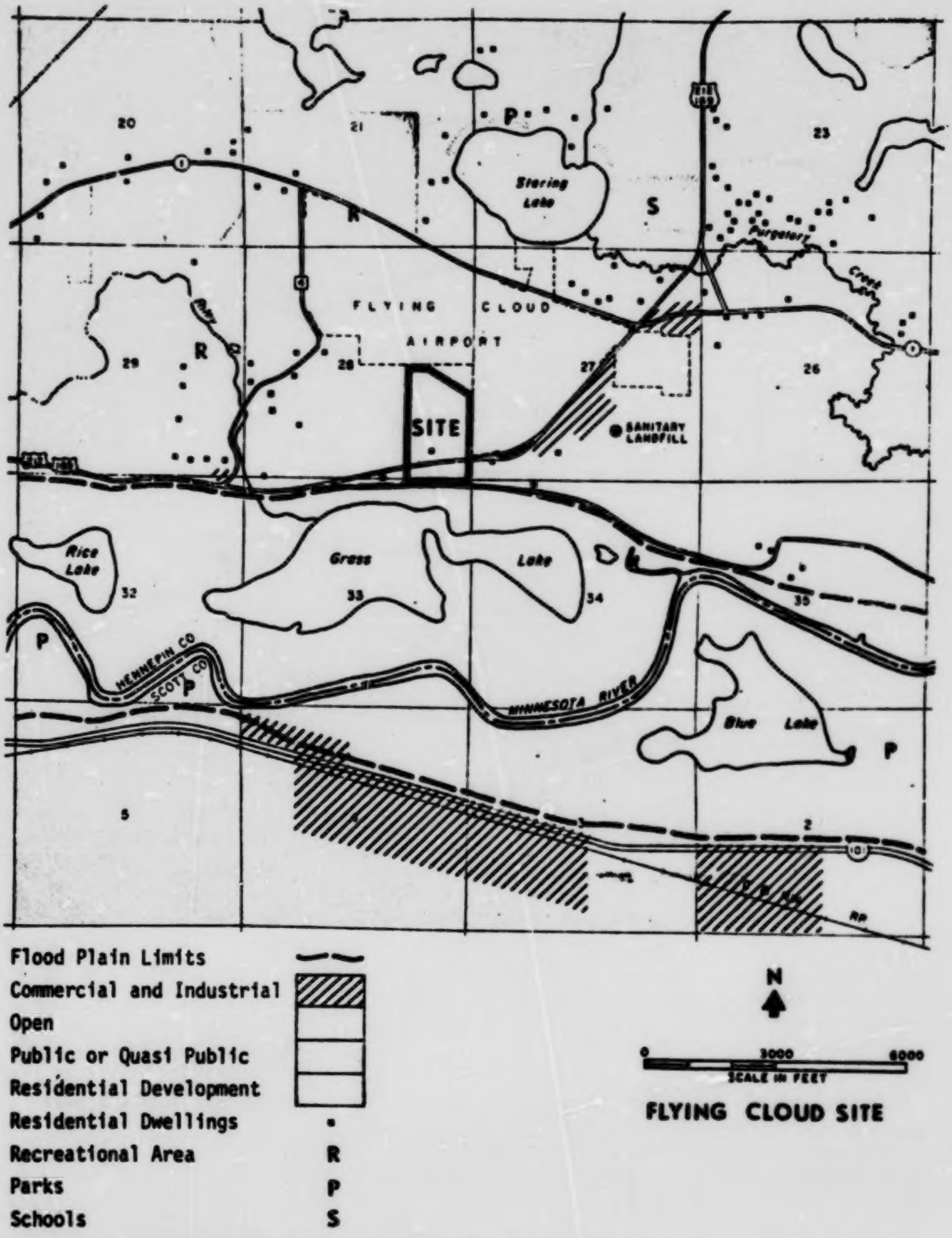

20
21
23
P
Staring Lake
S
169
R
Purgatory Creek
FLYING CLOUD AIRPORT
29
R
28
27
26
SITE
SANITARY LANDFILL
169
Rice Lake
32
Grass
33
Lake
34
35
P
HENNEPIN CO
SCOTT CO
P
MINNESOTA RIVER
Blue Lake
P
5
4
3
2
101
RR
Flood Plain Limits
Commercial and Industrial ▨
Open
Public or Quasi Public
Residential Development
Residential Dwellings •
Recreational Area R
Parks P
Schools S
N
0
3000
6000
SCALE IN FEET
FLYING CLOUD SITE

Figure 2. FLYING CLOUD SITE. Existing Land Use.

Source: Barr Engineering Co. Minneapolis[3]

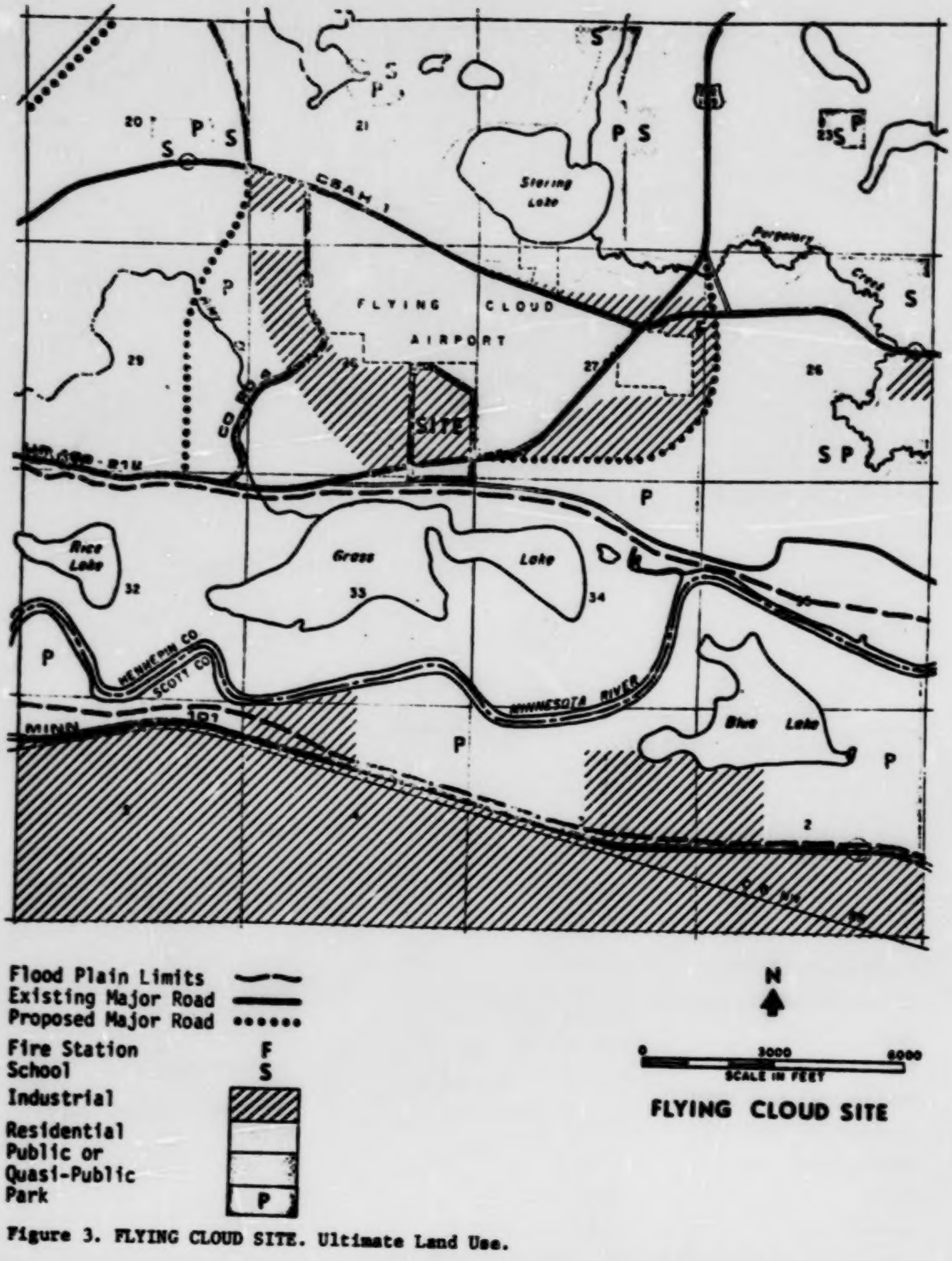

S
P S
20
21
P S
S P
CSAH 1
Staring Lake
Purgatory Creek
P
FLYING CLOUD AIRPORT
29
28
27
26
SITE
S P
P
Rice Lake
32
Grass Lake
33
34
P
HENNEPIN CO
SCOTT CO
MINNESOTA RIVER
Blue Lake
P
P
2
Flood Plain Limits
Existing Major Road
Proposed Major Road
Fire Station F
School S
Industrial
Residential
Public or Quasi-Public
Park P
N
0
3000
6000
SCALE IN FEET
FLYING CLOUD SITE

Figure 3. FLYING CLOUD SITE. Ultimate Land Use.

Source: Barr Engineering Co. Minneapolis[3]

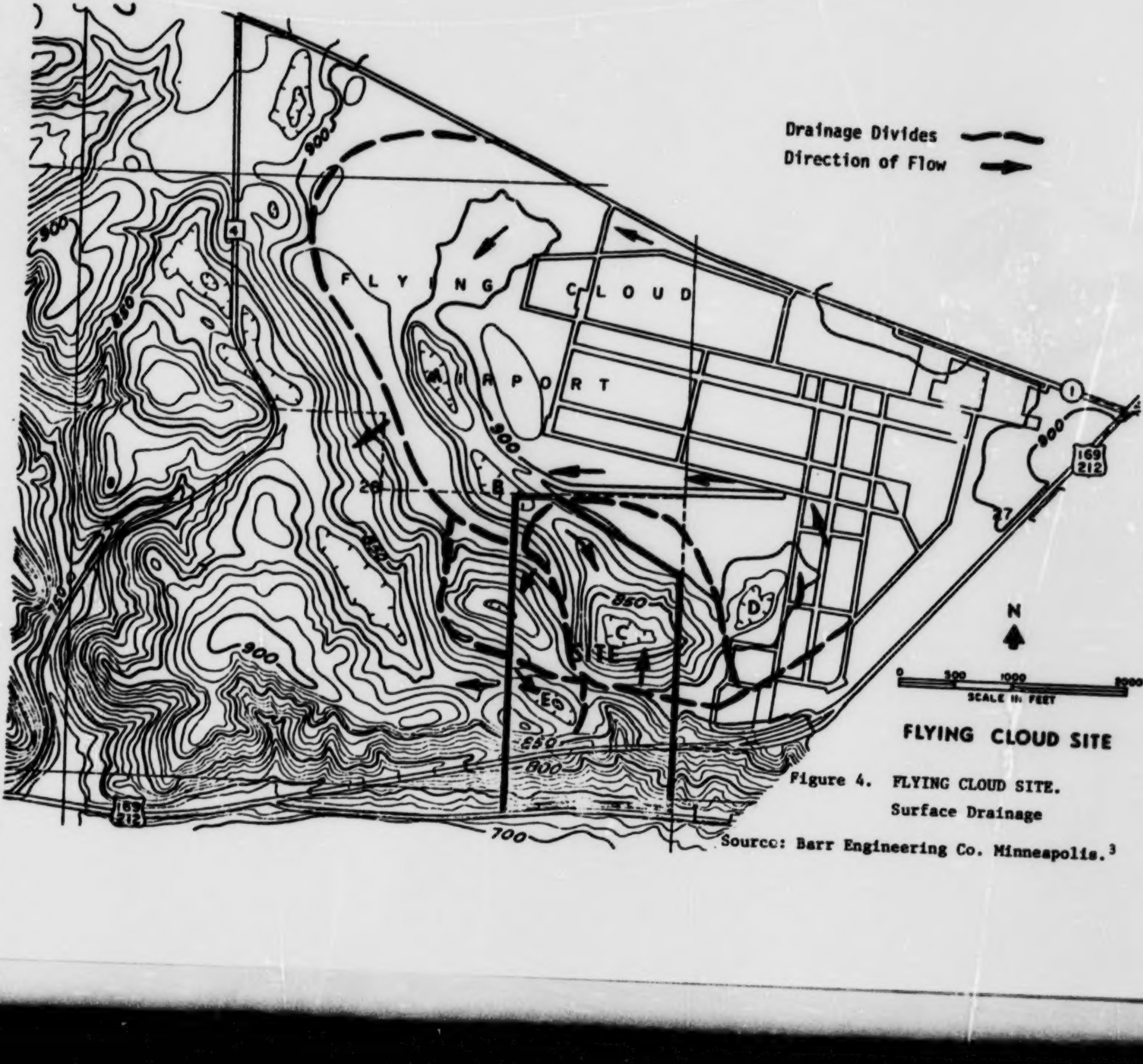
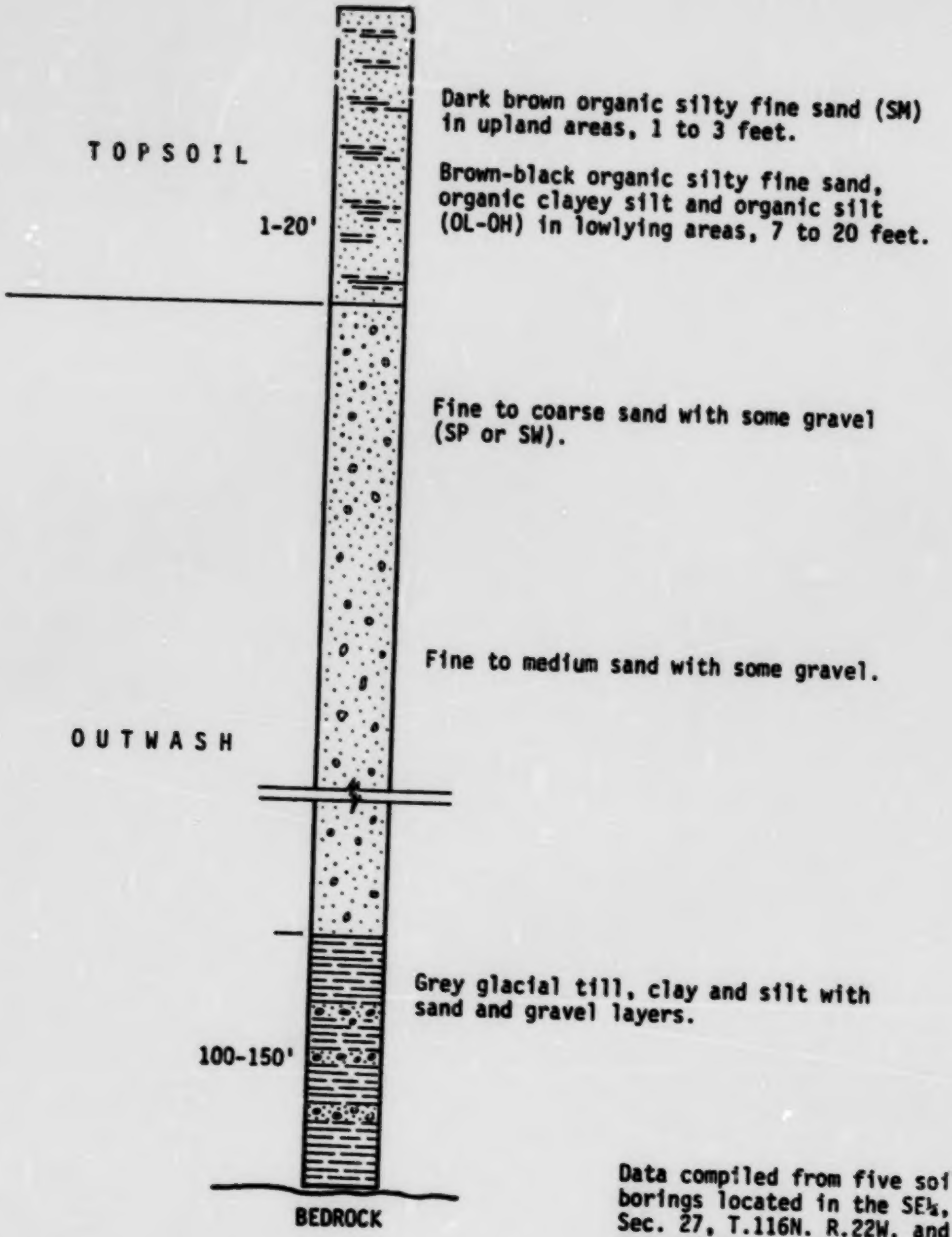

Drainage Divides
Direction of Flow
FLYING CLOUD AIRPORT
SITE
B
C
D
E
900
850
800
700
26
27
4
1
169 212
N
0
500
1000
2000'
SCALE IN FEET
FLYING CLOUD SITE

Figure 4. FLYING CLOUD SITE.
Surface Drainage

Source: Barr Engineering Co. Minneapolis.[3]


TOPSOIL
1-20'
Dark brown organic silty fine sand (SM) in upland areas, 1 to 3 feet.
Brown-black organic silty fine sand, organic clayey silt and organic silt (OL-OH) in lowlying areas, 7 to 20 feet.
Fine to coarse sand with some gravel (SP or SW).
Fine to medium sand with some gravel.
OUTWASH
Grey glacial till, clay and silt with sand and gravel layers.
100-150'
BEDROCK

Data compiled from five soil borings located in the SE¼, Sec. 27, T.116N. R.22W. and approximately 3,600 feet east of the proposed site.

Figure 5. FLYING CLOUD SITE. Typical Soil Profile

Source: Barr Engineering Co. Minneapolis[3]

an impermeable synthetic liner (such as hypalon, polyvinyl chloride, or rubber) positioned in the bottom of each disposal cell (Figure 6). This barrier will be protected by a layer of permeable washed sand. A network of perforated pipes will be positioned immediately above the primary liner to facilitate leachate collection. A secondary barrier of compacted colloidal clay will underline the primary barrier and serve to further protect the groundwater if the primary barrier should fail. The secondary barrier will also be served by a separate leachate collection network. Discharge wells will be installed upgradient and downgradient of the site. These wells will serve as a third level of protection to control leachate plume movement in the very unlikely event that both the primary and secondary leachate management systems should simultaneously fail to perform.

The performance of the leachate management system and groundwater quality will be monitored at all times. The surveillance program will include suction lysimeters underneath the secondary barrier, core soil samples around the perimeter, and observation wells with continuously recording pH and conductivity probes. Groundwater and soil samples will be collected routinely and subjected to comprehensive laboratory analyses to determine the presence of leachate species. Monitoring will continue after the site is closed to assure long-term environmental protection.

Completed waste burial units will be capped with an impervious liner to minimize further infiltration from precipitation.

Surface runoff will be managed and collected on-site. No runoff will be discharged from the site without receiving quality analysis and wastewater treatment, if necessary. Runoff from uncontaminated or non-disposal areas will be collected in lined depressions. Surface runoff from disposal/treatment areas and leachate effluents from disposal units will be collected in separate lined holding basins. Contaminated effluents will be treated onsite by physical and chemical treatment techniques prior to being discharged to the Blue Lake activated sludge wastewater treatment plant for final treatment.

Waste from 12 major Standard Industrial Classifications (SIC) are generated in the Minneapolis/St. Paul area. Foremost among these industrial wastes are electroplating wastes, petroleum refining wastes, inorganic chemicals manufacturing wastes, and tannery wastes. Other industrial wastes such as metals mining wastes which are not immediately available within the service area, will be imported in sufficient quantities to demonstrate their landfilling potential.

The grantee has completed an initial inventory of waste generated in the service area and will augment this data with additional inventory data to formulate the facility's design engineering plan. The overall process design proposed by the Minnesota PCA emphasizes quality control to assure safe waste handling, treatment, and disposal (Figure 7). Waste receiving techniques, including sample analysis, and storage areas, will assure that noncompatible wastes are segregated throughout the entire waste handling, treatment, and disposal process. Employee health monitoring programs and safety equipment will be provided to assure a safe work environment. For example, chemical firefighting equipment will be available to control accidental fires.

Chemical waste disposal decisions will include consideration of the waste's:

. chemical form (inorganic or organic)

. persistence

. acute or chronic toxicity

. genetic effect

. flammability/reactivity

Several waste preparation and treatment techniques have been proposed including: encapsulation, blending, neutralization, fixation, and liquid-solids separation (such as coagulation and flocculation). These techniques will be further evaluated during the facility design phase of the demonstration program. Waste preparation techniques selection criteria will emphasize:

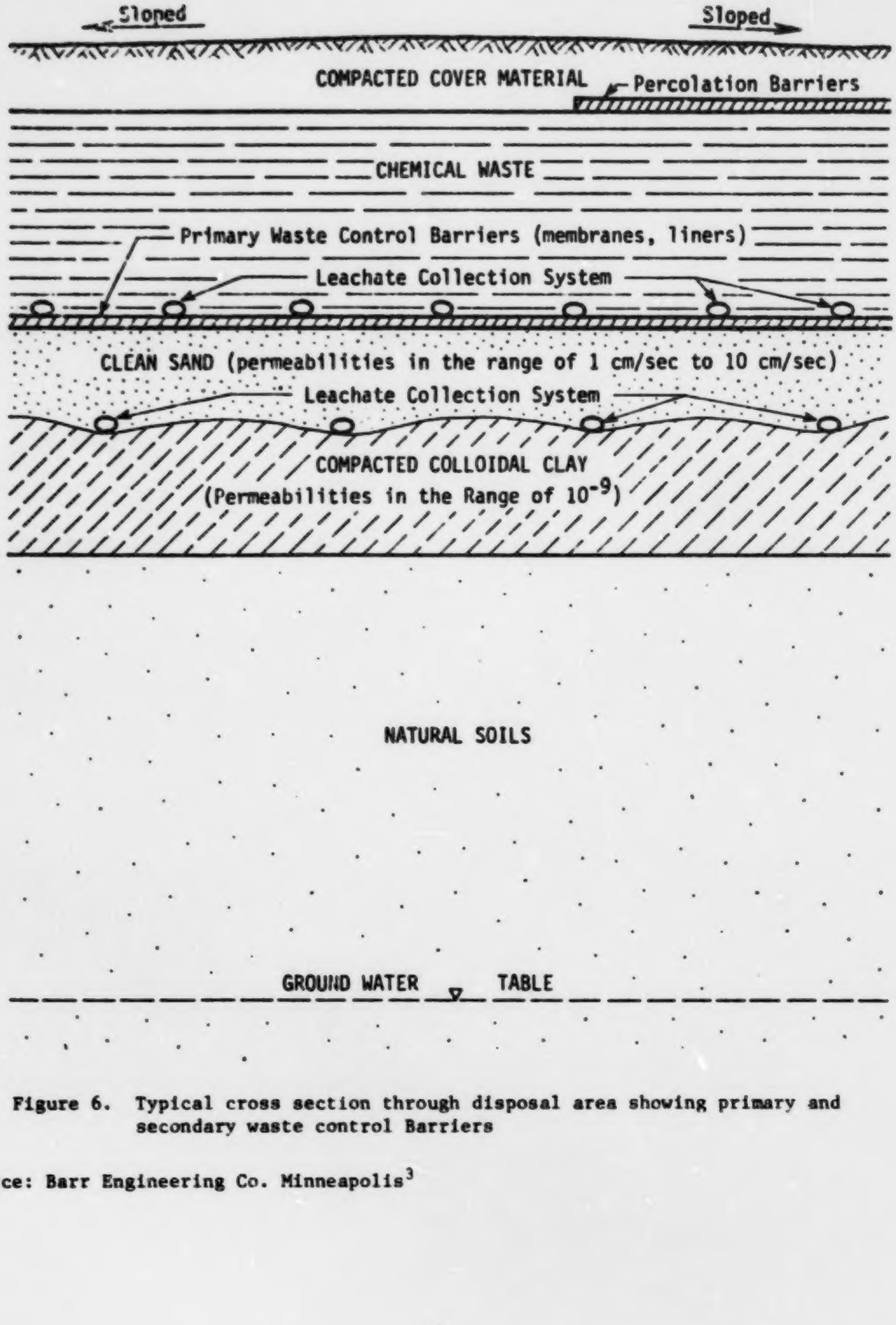

Sloped
Sloped
COMPACTED COVER MATERIAL
Percolation Barriers
CHEMICAL WASTE
Primary Waste Control Barriers (membranes, liners)
Leachate Collection System
CLEAN SAND (permeabilities in the range of 1 cm/sec to 10 cm/sec)
Leachate Collection System
COMPACTED COLLOIDAL CLAY
(Permeabilities in the Range of 10^-9)
NATURAL SOILS
GROUND WATER ▽ TABLE

Figure 6. Typical cross section through disposal area showing primary and secondary waste control Barriers

Source: Barr Engineering Co. Minneapolis[3]

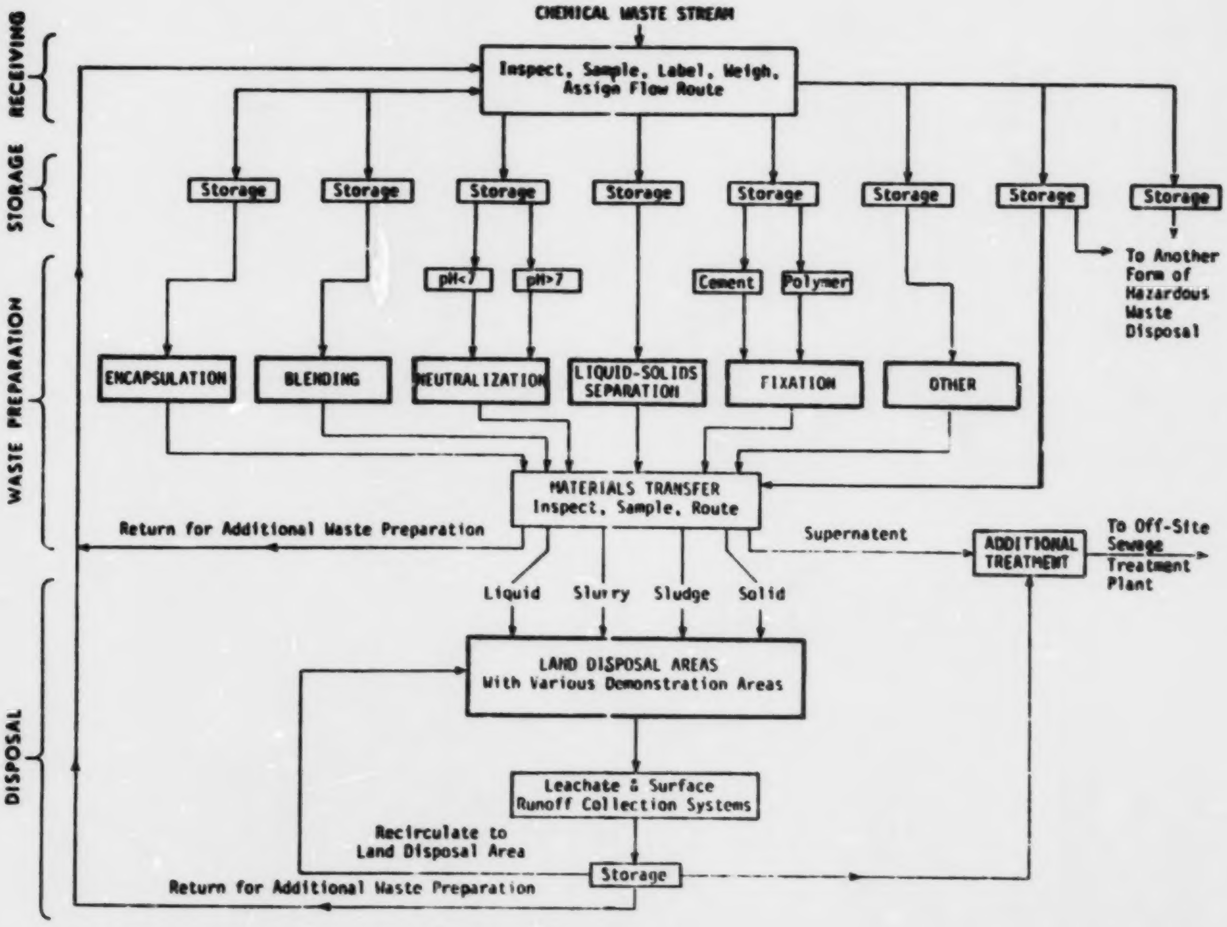

CHEMICAL WASTE STREAM
Inspect, Sample, Label, Weigh, Assign Flow Route
RECEIVING
STORAGE
WASTE PREPARATION
DISPOSAL
Storage
Storage
Storage
Storage
Storage
Storage
Storage
Storage
pH<7
pH>7
Cement
Polymer
To Another Form of Hazardous Waste Disposal
ENCAPSULATION
BLENDING
NEUTRALIZATION
LIQUID-SOLIDS SEPARATION
FIXATION
OTHER
MATERIALS TRANSFER Inspect, Sample, Route
Return for Additional Waste Preparation
Supernatent
ADDITIONAL TREATMENT
To Off-Site Sewage Treatment Plant
Liquid
Slurry
Sludge
Solid
LAND DISPOSAL AREAS With Various Demonstration Areas
Leachate & Surface Runoff Collection Systems
Recirculate to Land Disposal Area
Storage
Return for Additional Waste Preparation

Figure 7. Disposal facility chemical waste flow.

Source: Barr Engineering Co. Minneapolis. [3]

- economy of scale, i.e., techniques that have applicability to a broad range of waste types
- volume reduction to efficiently use available landfill space and eliminate initial water content
- compatibility to the waste types and forms generated in the service region

Waste inventories, both storage and burial inventories, and burial maps will be maintained by the landfill operator. With such inventories, it will be feasible to locate and extract any given waste with minimal searching. This procedure will facilitate future waste reclamation or site repair efforts.

Technical methods, project results and recommendations will be reported on by the grantee at the conclusion of the five-year grant program. Two interim reports, submitted at the conclusion of the project's second year, will discuss:

1. Site selection, site purchase, baseline data gathering, and licensing tasks. Initial phases of the citizen acceptance campaign will also be discussed.

2. Waste inventory findings, process selection and design, environmental surveillance design and other facility design tasks. The report will also project the environmental impact of the facility's design and operational procedures, including: liner integrity, waste compatibility, leachate management system effectiveness, surveillance network effectiveness, and contingency plans to handle system failures or spills. This will serve to update the Environmental Impact Assessment prepared as part of the grant application.

All interim and final reports will be published by EPA and made available.

OTHER HAZARDOUS WASTE MANAGEMENT PROJECTS

The Office of Solid Waste Management Programs conducts a variety of studies and demonstrations designed to provide data base and support for the formulation of guidelines for the treatment and disposal of hazardous wastes. Subject areas include (1) investigation of pollution incidents to determine causes and magnitude of damages, (2) identification and quantification of potentially hazardous wastes, (3) evaluation and demonstration of adequate treatment and disposal techniques, and (4) investigation of a variety of implementation oriented issues such as economic impacts.

Some are demonstration projects like the Chemical Waste Landfill project. In addition, two projects have been undertaken to demonstrate destruction of hazardous wastes by incineration. Versar, Incorporated has completed a series of test burns in which the destruction of DDT and 2,4,5-T pesticides was demonstrated in conjunction with the burning of sewage sludge.[4] The demonstration facility was the multiple hearth municipal sewage treatment facility in Palo Alto, California. Destruction ratios in excess of 99.9 percent were consistently achieved. A more ambitious project is now underway in which sixteen representative industrial wastes will be test destructed under varying conditions in seven commercial scale incinerators.[5] The facilities chosen represent design variations which are currently available. The second test sequence is now underway. Total funding is approximately 1.5 million dollars. TRW Systems Group and Arthur D. Little, Incorporated are handling the sampling and analysis, and waste acquisition and facility availability are being subcontracted.

Other projects include contract studies and field investigations. Table 1 summarizes these programs. Additional information is available from the Project Officers. The Appendix identifies OSWMP sponsored publications on the subject of hazardous waste management which can be easily obtained.

TABLE 1. OSWMP HAZARDOUS WASTE PROJECTS

Project	Type	Subject	Project Officer	Contractor	Completion
Chemical Waste Landfill	Grant	Demo.	Farb	Minnesota	June, 1980
Standard Attenuation Proc.	Contract	Study	Lindsey	(Not Awarded)	April, 1977
Incineration Eval.	Contract	Demo.	Schaum	TRW	January, 1977
Treatment Process Analysis	Contract	Study	Crumpler	A.D. Little	July, 1976
Alternative Treatment Studies					
Organic Chemical Industry Wastes	Contract	Study	Crumpler	(Not Awarded)	November, 1976
Petroleum Refinery Wastes	Contract	Study	Crumpler	(Not Awarded)	November, 1976
Metals Refining Industry Wastes	Contract	Study	Tarnay	(Not Awarded)	February, 1977
Inorganic Chemicals Industry Wastes	Contract	Study	Tarnay	(Not Awarded)	February, 1977
Pesticide Incineration Study	Contract	Demo.	Schaum	Versar	March, 1975
Groundwater Sampling Study	Contract	Field Investigation	Huber	(Not Awarded)	January, 1978
Standard Leaching Test	Intra Agency	Research	Lazar	EPA-Edison	March, 1977
Pesticide Chemical Disposal	Contract	Study	Trask	TRW	January, 1976
Energy Recovery	Contract	Study	Corson	Reynolds, Hill, Smith	October, 1976
Capacity Creation, Waste Industry	Contract	Study	Kohan	E.D. Snell	February, 1976
Container Landfill Analysis	Contract	Study	Day	TRW	January, 1976
Economic Analysis, Inorganic Chemical and Petroleum Industries	Contract	Study	Shannon	A.D. Little	April, 1976
Industry Studies					
Primary & Storage Batteries	Contract	Study	Fields	Versar	January, 1975
Industrial Inorganic Chemicals	Contract	Study	Fields	Versar	March, 1975

Table 1 Continued

Project	Type	Subject	Project Officer	Contractor	Completion
Industry Studies (cont.)					
Pharmaceuticals	Contract	Study	Pearce	A.D. Little	January, 1976
Metals Mining	Contract	Study	Pearce	Midwest Research	May, 1976
Paint & Allied Products	Contract	Study	Straus	WAPORA	January, 1976
Petroleum Refining	Contract	Study	Straus	Jacobs Engineers	March, 1976
Organic Chemicals	Contract	Study	Fields	TRW	January, 1976
Electroplating	Contract	Study	Straus	Battelle	February, 1976
Primary Metals	Contract	Study	Pearce	Calspan	April, 1976
Textile Mill Products	Contract	Study	Straus	Versar	April, 1976
Rubber and Plastics	Contract	Study	Straus	F.D. Snell	April, 1976
Leather Tanning/Finishing	Contract	Study	Pearce	SCS	May, 1976
Special Machinery	Contract	Study	Pearce	WAPORA	April, 1976
Oil Refining	Contract	Study	Straus	(Not Awarded)	May, 1976
Waste Exchange Analysis	Contract	Study	Porter	A.D. Little	July, 1976

REFERENCES

1. U.S. Environmental Protection Agency, Office of Solid Waste Management Programs. Hazardous waste disposal damage reports. Environmental Protection Publication SW-151. Washington, U.S. EPA, June 1975.

2. U.S. Environmental Protection Agency, Office of Solid Waste Management Programs. Disposal of hazardous wastes; report to Congress. Environmental Protection Publication SW-115. Washington, U.S. Government Printing Office, 1974. 110 p.

3. State of Minnesota demonstration grant application - chemical waste land disposal facility. Minneapolis, Barr Engineering Co., 1975. 286 p.

4. Whitmore, F.C., and R.L. Durfee. A study of pesticide disposal in a Sewage sludge incinerator. Unpublished report to the Environmental Protection Agency. Springfield, Va., Versar Inc., 1975. 174 p.

5. TRW Systems, Inc. Destructing chemical wastes in commercial scale incinerators; technical summary. Unpublished report to the Environmental Protection Agency. Redondo Beach, Ca., TRW Systems, Inc., July 1975. 139 p.

APPENDIX

HAZARDOUS WASTE PUBLICATIONS

1. Disposal of Hazardous Wastes; Report to Congress. U.S. EPA, Office of Solid Waste Management Programs. Environmental Protection Publication SW-115. Washington, U.S. Government Printing Office, 1974. 110 p. Available from OSWMP (#345).*

2. Federal Program for Hazardous Waste Management. J.P. Lehman. *Waste Age*, 5(6):6-7, 66-68, Sept. 1974. Available from OSWMP (#399).

3. Hazardous Wastes. Environmental Protection Publication SW-138. Washington, U.S. Government Printing Office, 1975. 24 p. Available from OSWMP (#450).

4. Environmental Information; Hazardous Wastes and their Management. Washington, U.S. Environmental Protection Agency, May 1975. 3 p. Available from OSWMP (#452).

5. Pesticides; EPA Proposal on Disposal and Storage. *Federal Register*, 39(200): 3687-36950, Oct. 15, 1974. Available from OSWMP (#398).

6. Where Have All the Toxic Chemicals Gone? W.H. Walker. *Ground Water*, 11(2):11-20, Mar.-Apr., 1973. Available from OSWMP (#415).

7. One Private Plant Treats Oil, Chemical Residues in Denmark. P. Henriksen. *Solid Waste Management*, 17(5):77-78, 139, May 1974. Available from OSWMP (#418).

8. Incineration in Hazardous Waste Management. A.C. Scurlock, A.W. Lindsey, T. Fields, Jr., and D.R. Huber. Environmental Protection Publication SW-141. Washington, U.S. EPA, 1975. 104 p. Available from OSWMP (#427).

9. Hazardous Waste Management Facilities in the United States. A.J. Hayes. Environmental Protection Publication SW-146. Washington, U.S. EPA, Dec. 1974. 39 p. Available from OSWMP (#429).

10. Hazardous Waste Disposal Damage Reports. Environmental Protection Publication SW-151. Washington, U.S. EPA, June 1975. 8 p. Available from OSWMP (#449).

11. Industrial Waste Management; Seven Conference Papers. Environmental Protection Publication SW-156. Washington, U.S. EPA, Feb. 1975. 111 p. Available from OSWMP (#453).

12. Organic Pesticides and Pesticide Containers; A Study of their Decontamination and Combustion. R.C. Putnam, F. Ellison, R. Protzmann, and J. Helonsky. Environmental Protection Publication SW-21c. U.S. EPA, 1971. 175 p. Available from NTIS (#PB-202 202). Cost $6.25.

13. A Study of Hazardous Waste Materials, Hazardous Effects and Disposal Methods. Booz Allen Applied Research, Incorporated, U.S. EPA, 1973. 3v. (vol. 1 - 408 p., vol. 2 - 544 p., vol. 3 - 400 p.). Available from NTIS (#PB-221 465 - $10.50, #PB-221 466 - $12.50, #PB-221 467 - $11.50.

14. Tentative Procedure Analyzing Pesticide Residues in Solid Waste. R.A. Carnes. U.S. EPA, 1972. 23 p. Available from NTIS (PB-222 165). Cost $3.25.

15. Public Attitudes Towards Hazardous Waste Disposal Facilities. L.L. Lackey et al. U.S. EPA, 1973. 181 p. Available from NTIS (#PB-223 638). Cost $7.00.

16. Recommended methods of reduction, neutralization, recovery or disposal of hazardous waste. R.S. Ottinger et al. U.S. EPA, 1973. 16 v. Available from NTIS.

    PB-224 580 v.1. Summary report. 210 p. ($7.25)
    PB-224 581 v.2. Toxicologic summary. 224 p. ($7.50)
    PB-224 582 v.3. Ultimate incineration. 251 p. ($8.50)
    PB-224 583 v.4. Miscellaneous waste treatment processes. 149 p. ($5.75)
    PB-224 584 v.5. Pesticides and cyanide compounds. 146 p. ($5.75)

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* Shelf number

PB-224 585 v.6. Mercury, arsenic, chromium and cadmium compounds. 207 p. ($7.25)

PB-224 586 v.7. Propellants, explosives, and chemical warfare material. 266 p. ($7.50)

PB-224 587 v.8. Miscellaneous inorganic and organic compounds. 79 p. ($4.75)

PB-224 588 v.9. Radioactive materials. 168 p. ($6.25)

PB-224 589 v.10. Organic compounds. 316 p. ($9.25)

PB-224 590 v.11. Organic compounds (continued). 247 p. ($7.50)

PB-224 591 v.12. Inorganic compounds. 330 p. ($9.50)

PB-224 592 v.13. Inorganic compounds (continued). 290 p. ($8.75)

PB-224 593 v.14. Summary of waste origins. 160 p. ($6.25)

PB-224 594 v.15. Research and development plans. 109 p. ($5.25)

PB-224 595 v.16. References. 424 p. ($10.50)

17. Alternatives to the Management of Hazardous Wastes at National Disposal Sites. Arthur D. Little, Inc. Environmental Protection Publication SW-46c. U.S. EPA, 1973. 85 p. Available from NTIS (#PB-225 164). Cost $4.75.

18. Program fro the Management of Hazardous Wastes. Battelle Memorial Institute. U.S. EPA, 1974. 2 v. (Vol. 1 - 385 p., vol. 2 - 778 p.). Available from NTIS (#PB-233 630 - $10.25, #PB-233 631 - $17.25).

19. Promising Technologies for Treatment of Hazardous Wastes. R. Landreth and C. Rogers. U.S. EPA, 1974. 44 p. Available from NTIS (#PB-238 145). Cost $3.75.

20. Assessment of Industrial Hazardous Waste Practices, Storage and Primary Batteries Industries. Versar, Inc. Environmental Protection Publication SW-102c. U.S. EPA, Jan. 1975. 209 p. Available from NTIS (#PB-241 204). Cost $7.25.

21. Assessment of Industrial Hazardous Waste Practices, Inorganic Chemicals Industry. Versar, Inc. U.S. EPA, Sept. 1975. Available from NTIS (#PB-244 832). Cost $12.25.

22. State Program Implementation Guide: Hazardous Waste Surveys. C.H. Porter. Environmental Protection Publication SW-160. Washington, U.S. EPA, July 1975. 38 p. Available from OSWMP (#464).

23. Information About Hazardous Waste Management Facilities. D. Farb and S.D. Ward. Environmental Protection Publication SW-145. Washington, U.S. EPA, July 1975. 130 p. Available from OSWMP (#468).

24. Tetrachlorodibenzodioxin: An Accidental Poisoning Episode in Horse Arenas. C.D. Carter, R.D. Kimbrough, J.A. Liddle, R.E. Cline, M.M. Zack, Jr., W. F. Barthel, R.E. Koehler, and P.E. Phillips. Science 188(4189):738-740, May 16, 1975. Available from OSWMP (#474).

25. Landfill Disposal of Hazardous Wastes: A Review of Literature and Known Approaches. T. Fields, Jr. and A.W. Lindsey. Environmental Protection Publication SW-165. Washington, U.S. EPA, Sept. 1975, 36 p. Available from OSWMP (#475).

26. Ultimate Disposal of Spilled Hazardous Materials. A.W. Lindsey. Chemical Engineering, Oct. 27, 1975. Soon to be available from OSWMP.

27. Chemical Waste Land Disposal Facility Demonstration Grant Application. Minnesota Pollution Control Agency. Environmental Protection Publication SW-87d. Washington, U.S. EPA. Soon to be available from NTIS.

PUBLICATION SOURCES

- OSWMP publications can be obtained by contacting:

  Solid Waste Information Materials
  Control Section
  U.S. Environmental Protection Agency
  Cincinnati, Ohio 45268

  (please indicate three digit shelf no.)

- NTIS publication can be obtained by contacting:

  National Technical Information Service
  U.S. Department of Commerce
  Springfield, Virginia 22161

  (please indicate PB number)

HAZARDOUS WASTE GUIDELINES: PLANS AND PROSPECTS

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ABSTRACT

Current Federal legislation authorizes EPA to issue both advisory guidances and guidelines (which are mandatory for Federal facilities) related to solid waste management systems. In addition, pending Congressional legislation contemplates a more regulatory approach to hazardous waste management based upon a permit system operated primarily at the State level.

This paper outlines the scope and tentative schedule for solid waste guidance/guideline issuances. It defines the nature of these issuances and contrasts them with the EPA air and water regulatory approaches. In addition, the effect of pending legislation is analyzed in the context of the current guideline/guidance plans.

It is a particular pleasure for me to participate in this conference on land disposal of hazardous waste in the "orientation" portion of the program. For as essential as land deposition is to any future waste management planning, it must be viewed within the overall context of complementary options and alternatives. Thus, from the technical assistance perspective of EPA, the opportunity to communicate with the research community as to the direction of our current guidance/guideline programs is very important.

Not only does it afford us an occasion to assess the match between on-going research efforts and current Agency guidance/guideline plans, but also a chance for dialogue as to what future gaps need to be filled if effective guidances are to be issued.

The cornerstone of current OSWMP guidance/guidelines programs is the Solid Waste Disposal Act, as amended (SWDA). The critical sections of this Act relative to hazardous waste bear some review as the opportunities for formal guidance in it are several.

Section 212 of the Act was the origin of EPA's now familiar Report to Congress; Disposal of Hazardous Wastes. Submitted to Congress in June 1973, the Report was our first major assessment of the seriousness of the hazardous waste problem. Among its major conclusions were that (1) hazardous waste legislation was a key to solution of the problem of mismanaged wastes and (2) national disposal sites were not a viable waste disposal strategy, given the available fledgling industry in this field. In addition, the President submitted the Hazardous Waste Management Act for consideration by Congress in February 1973, because of the significance of this issue.

Section 204(a) of the SWDA Act carries basic research, demonstration, and training mandates. Much of the health and environmental effects work, disposal operation investigations, materials and energy recovery work, and waste system studies now underway are authorized under this section.

Section 204(b) instructs EPA to collect information and make it available through publications and other means, to cooperate with public and private groups, and to make grants. This part of Section 204 is significant to our guidance promulgation efforts, and I shall return to it.

The mandate for guidelines for recovery, collection, separation, and disposal systems is contained in Section 209. Such guidelines under Section 209(a) are recommended to government agencies at all levels - not just Federal ones. Section 209(b) calls for model codes, ordinances, and statutes as well as issuance of data on costs of constructing, operating, and maintaining technically feasible methods for collection, separation, disposal, recovery, and recycling.

Finally, Section 211 of the SWDA adds some "teeth" to the otherwise advisory guidelines under Section 209(a), in that all Federal agencies shall ensure compliance with such guidelines issued under that section. You may be familiar with some of the results of such guidelines. For example, the Bureau of Land Management has recognized the EPA Guidelines on Thermal Processing and Land Disposal of Solid Waste (Federal Register, May 14, 1974) as well as the Recommended Procedures for Disposal and Storage of Pesticides and Pesticide Containers (Federal Register, May 1, 1974) (also published by OSWMP) as the minimum requirements for use of BLM lands for waste disposal.

In summary, the current authorities of interest here are Section 204(b)--the issuance of recommendations--and Sections 209(a) and (b)--guideline issuances and model ordinance drafting, respectively.

Before addressing our plans for hazardous waste guideline development, some definitions and clarifications are in order. First, many of you are familiar with the word "guideline" in the context of Federal Water Pollution Control Act (FWPCA) where "effluent limitation guidelines" (ELG) are to be set in accordance with best practicable or best available technologies. Thus, the ELG for an industry sector is, in reality, an enforceable permit requirement, not just technical advice as is the case with solid waste guidelines. The only persons for whom solid waste guidelines are mandatory are Federal agencies; for all others, they are advisory. Thus, the word "guideline" has a unique meaning in the solid waste legislation.

A second issue of definition relates to the focus in the FWPCA, as amended, and the Clean Air Act, as amended, (CAA) on performance standards. That is, the standards or goals to be met by a potentially polluting activity should be specified rather than the process or technology to be used. We concur with this approach as it leaves technological options open and encourages development of new techniques.

Finally, one major contrast between the FWPCA and CAA mandates and the approach in solid waste bears review. Both the air and water laws require industry-by-industry standards relating to stationary emissions. That is, specific levels of discharge to the air and water environment are to be set for each industry sub-segment. In contrast to this legally required strategy, those dealing with industrial wastes know that they can be (and often are) shipped to treatment/disposal facilities. In addition, the solid waste statute refers to systems and methods without reference to industry segments. As a result, the current thrust of our guidance/guideline development efforts is on pathways that wastes follow and the systems governing their flow.

What then are our plans to develop guidances and guidelines? For ease of discussion, we have defined the word "guidance" as advice issued by EPA in the Federal Register under the authority of Sec. 204 of the Solid Waste Disposal Act. Such guidance represents the Agency's best technical counsel on an issue related to hazardous waste management systems or pathways; it does not have regulatory status.

Guidelines are advice issued by the Agency in the Federal Register under the authority of Sec. 209. Although only advisory to everyone else, Section 211 makes Sec. 209(a) issuances mandatory for Federal facilities. Again, the guideline represents our best technical advice, but due to its impact on Federal facilities, much more extensive impact analysis and interagency review are necessary than are needed for guidances.

"System operations" guidances refer generally to the flow of wastes from generator to storage, treatment, and ultimate disposal. Potential subject areas are many in number, but those in which the States and others seem most interested at present are waste transport control (through trip-ticketing), wastes compatibility guides, facilities management suggestions, site selection methodology, etc. "Pathway" guidances would provide typical performance specifications for incinerators, chemical waste landfills, and chemical treatment processes. As an example, an incinerator guidance would describe for the person who has chosen incineration as his disposal option, the optimum temperature, dwell time, and turbulence characteristics for the waste type he has selected. Obviously, our recommendation of such minimum levels would be based on test burn experiences with wastes of the same or similar kind from which we had extrapolated.

Our strategy under current legislation has two phases. First, issue system operation and pathway guidances under Section 204 as soon as practicable. This approach allows us (1) to make Federal policy known to a very broad audience (including industry), (2) to address our technical assistance obligations to the States in a priority way, and (3) to signal industry and the States as to our intentions, if stronger Federal authorities should come about.

A second part of our strategy is to simultaneously explore the breadth and extent of the hazardous waste management problem among Federal agencies. To the extent that specific problems are serious enough and have not been addressed through adherence to the guidances, Sec. 209 guidelines could then be issued.

Exhibit I is an interim plan for the issuance of guidances and guidelines under Solid Waste Disposal Act. It describes our schedule for guidance/guideline issuance over the next several fiscal years. Like all good plans, it is subject to change. It does, however, give a sense as to when we expect the results of several technical studies to be sufficient to issue advice.

Special comment regarding the column marked Recommended Procedures is warranted. Such a procedure will represent our best technical counsel on a very specific problem (such as disposal of wastes contaminated with a certain chemical) or advice on a specific industry stream. The procedures will be notable for their lack of widespread applicability to many waste generators and disposers and/or their very specific focus on single waste streams. Such issuances are contemplated, for example during FY 76 regarding PCB-contaminated waste and during FY 78 regarding the tradeoffs of various treatment methods for some streams in the organic chemical and petroleum refining industries.

Of special interest to this group would be our plan to use the fruits of our chemical waste landfill demonstration project along with other results in FY 79 to address waste-loading limits for landfill sites and chemical waste landfill design.

With the long time frame on this interim plan, the question of future Federal legislative initiatives becomes very relevant. As you may know, the Senate Committee on Public Works has a bill numbered S.2150 which has been the subject of considerable public dialogue for over a year. On December 15, 1975, the House Subcommittee on Transportation and Commerce issued a staff print of a Solid Waste Utilization Act for public comment. Thus, both Houses of Congress appear to be ready to address the issues of waste management, including hazardous wastes, in specific terms.

The concepts included in both of these legislative initiatives with regard to hazardous waste are very similar. First, there are special sections of these comprehensive drafts devoted to hazardous wastes. Second, the Administrator must define or identify hazardous wastes within certain time frames in the drafts in both Houses. Third, a program for the permitting of the storage, treatment, and disposal is mandated in both drafts; the House version also recognizes generator reporting obligations and the importance of the transportation link to effective management. Both drafts recognize operational, technical, institutional, and economic requirements for permit holders through permit conditions.

Additionally, both drafts suggest State implementation of such a permitting effort via approved Federal programs, and outline monetary disincentives in terms of withdrawn

Federal grant funds if the States do not assume the program. In the case of the House draft, only funds supporting the implementation of a hazardous waste program would be withdrawn instead of all State implementation money as in S.2150.

Even with this generalized overview, I think you can see the match between our current activities and prospective legislative initiatives. Almost all of the guidances that we have suggested could be translated into decision tools and/or specifications for Federal of State permit writers.

For that reason, we feel there is much to be gained from the early dialogue that will take place concerning guidance issuances. Not only the research community, but also industry, labor, public interest groups, and the academic community interested in effective hazardous waste management will be better able to focus their effort if Federal policy is clear and an open subject for continuing discussion in the months ahead.

Thank you very much.

Prospective

Hazardous Waste Management *Federal Register* Issuances

	Guidance (Sec. 204)	Recommended Procedure (Sec. 204)	Guideline (Sec. 209
FY 76	Policy Statement on HW Mgt.	Disposal of PCB-containing Wastes	
	Site Selection Criteria	Disposal of VC-containing Aerosol Cans	
FY 77	Waste Transportation Mgt. (Manifest Systems)		Model State HW Statute (Sec. 209 b)
	Compatability of HW at Disposal Facilities		
	Policy on Use of Public Lands for HW Facilities		
	Mgt. Aspects of HW Facilities (Insurance, Bonding)		
FY 78	Std. Sampling (and Analysis) for HW		
	State HW Mgt. Program - Resources and Organization		

Exhibit I (Continued)

FY 79 (cont'd)		
	Definition of HW (including Standard Leaching Test)	
	Reference Method for Evaluating Chemically Fixed Wastes	
		PCBTM* for Organic Chemical and Petroleum Industries
	Incineration Processes for HW	
FY 79	Determination of Loading Limit of Waste Sites	PCBTM* for Inorganic Chemicals and Metals Mining and Refining Industries
	Chemical Waste Landfill Design	

* PCBTM = Physical, Chemical, Biological Treatment Methods

DOCUMENTATION ON ENVIRONMENTAL EFFECTS OF POLLUTANTS

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ABSTRACT

To support their expected regulatory posture regarding the management and land disposal of hazardous wastes, the Office of Solid Waste Management Programs (OSWMP) is actively assembling an extensive scientific data base which must be considered if promulgated guidelines are to be scientifically sound and economically feasible. As part of that effort OSWMP has requested the Office of Research and Development (ORD) to develop from the existing literature a series of documents on the human health and ecological aspects associated with a number of selected pollutants--largely trace elements and pesticides. The reports are structured to be multimedia in scope, i.e., covering air, water, and land environments, and to assess the impact on life forms interacting with those environments. While each document is intended to be an authoritative compilation within the scope requested by OSWMP, no attempt has been made to establish or recommend environmental criteria levels. The format, component parts, and types of information being assessed will be described.

INTRODUCTION

The Solid and Hazardous Waste Research Division (SHWRD), as part of a program to identify and characterize hazardous wastes, is developing a series of comprehensive reports on specific aspects of a number of selected substances--largely trace metals and several organic entities. The substances chosen for inclusion in the "REEP" (Reviews of the Environmental Effects of Pollutants) program have been deemed hazardous and identified as components of waste streams destined for land disposal. The planned subjects for the REEP reports are: arsenic, asbestos, benzidine, beryllium, cadmium, chromium, copper, cyanides, DDT, endrin, fluorides, lead, mercury, methylparathion, PCB's, selenium, toxaphene, and zinc.

This paper is a brief overview of three aspects of the REEP program. The items to be discussed include:

1. Purpose and Use
2. Format and Scope
3. Some General Findings

PURPOSE AND USE

The REEP program was initiated in response to a need expressed by the Office of Solid Waste Management Programs (OSWMP) for comprehensive multimedia, multireceptor reports on selected pollutants. The REEP program, presently being developed under the authority of Sections 204 and 212 of the Solid Waste Disposal Act, as amended 1970, is to provide information support for OSWMP's anticipated regulatory posture regarding the proper management of hazardous waste materials, including handling and disposal. The documents developed under this program do not and are not intended to establish disposal criteria or recommended levels of pollutants in any media. They will, however, provide the user with part of a growing data base which must be considered if promulgated guidelines/standards for the storage, treatment, and land disposal of hazardous residuals are to be scientifically sound and economically feasible.

The reports present information on factors which influence the potential escape of pollutants from land disposal sites and review potential impacts of the subject pollutants on all media and life forms. More specifically, OSWMP expects the reports to:

1. provide an up-to-date compendium of information on toxicities (effects associated with exposures to specific substances contained in the air, water, and land media);
2. provide insight into the effective soil and plant indicators for detecting the presence of substances;
3. provide general data on the complexity, cost, and reliability of state-of-the-art analytical procedures for determining the presence of substances;
4. provide information on predictable reaction products of substances to aid in the design of criteria relating to mixing of wastes; and
5. permit assessment of the need for additional air emission standards due to the operational characteristics of hazardous waste treatment sites (1).

In addition to their designated user, the OSWMP, the reports developed under this program should be of value to other program offices within the Agency as both an information source and an identifier of knowledge gaps.

FORMAT AND SCOPE

As stated above, these reports are primarily concerned with the effects and transport of selected pollutants in the environment. Within the desired scope, each document is structured to be comprehensive although not necessarily encyclopedic. To facilitate the coverage of each topic a "modular" format was chosen. This format readily lends itself to constant literature review and updating, almost in a "loose leaf" fashion; and is directed at the individual with specific scientific interests and expertise. Topics which are covered and the general format of a REEP document are shown in Table 1. In general, representative studies are selected to be included in a REEP document. It should be noted that REEPs do not cover or discuss in detail anthropogenic sources, control technologies, or economic aspects of the subject pollutants. Much of this work is being conducted by other groups and programs within the Agency.

The REEP format allows information to be conveyed to two different audiences at two different levels. In fact, a REEP report could be considered to be two documents--an Executive Summary and a Detailed Report.

The first, a brief overview or "Executive Summary" (comprised of Chapter 1.0 of the REEP), is addressed primarily to the relatively nontechnical individual interested in a broad understanding of the subject. The second document (embracing Chapters 2-8) is aimed at individuals working in the area who are concerned with details and experimental approaches. The detailed chapters and sections of the reports are to provide the scientific basis for the Summary Chapter and constitute the referenced body of knowledge upon which OSWMP/EPA intends to establish its case for action in regard to the exercise or nonexercise of regulatory controls, and its defense of such actions in administrative or judicial proceedings. A description of the types of information considered in each chapter and the manner in which it is to be presented are given below.

Chapter 1.0--Summary

This chapter should present in clear and concise language the important findings, concepts, and relationships established in the scientific chapters and sections of the document. An individual reading Chapter 1.0 should gain a brief overview of information relevant to the potential for transport, movement, reactions in the environment, and health and ecological effects which might occur. Conclusions regarding the likelihood of environmental hazard and existing information gaps are presented as a conspicuous subdivision of Chapter 1.0. (See Table 1.)

The conclusions are numbered and usually consist of one to two sentences. No conclusions can be presented unless they are justified in the Summary of Findings subdivision of the Summary. (See Table 1.) Any information presented in the Summary of Findings subdivision should reference by section numbers the appropriate detailed chapter(s)/section(s) of the report from which it was drawn.

Chapter 2.0--Chemical and Physical Properties and Methods of Analysis

In this chapter, the characteristics of the pollutant are to be discussed from a viewpoint which establishes a relationship between properties and environmental significance of the pollutant. Esoteric chemical or physical properties, which can only be observed under extreme laboratory conditions and are environmentally unrealistic, are not germane to the discussion. On the other hand, information on chemical formulas and structures, physical states in the environment, stability and persistence, volatility, reactivity, solubility, and other properties of potential environmental importance is of interest. The discussion in Chapter 2.0 should be in relation to the pollutant's potential for transport and transformation in all media and impact on life forms. Reaction rates, thermodynamics, and other quantitative estimates of probability of movement, etc., are pertinent if they are environmentally feasible. Where specific examples do exist, the full ramifications and details should be presented in the proper chapter(s)/section(s) which follow. To effectively support the narrative discussion, tables containing formulas and properties of the pollutant are included.

Also included as part of this chapter are discussions relative to available techniques for measurement and analysis of the various environmentally significant forms of the subject pollutant. Specifically, some of the topics covered include relevant methods and their applications to air, water, sludge, and biological tissues, the sensitivity and reproducibility of the technique on routine use (upper and lower levels in sample being tested), problems encountered in sample preparation, selectivity of the method, and a general indication of the economy of the method.

Tables containing the above information help to summarize the data for the reader.

Chapters 3.0 through 6.0--Biological Aspects

The interactions of pollutants with a wide variety of life forms are covered in these chapters. A suggested approach to covering the biological information is shown in Table 1. The writers, however, do have some latitude in determining where to cover information on certain life forms. For example, some authors feel more comfortable including phytoplankton with the plants (Chapter 4.0) rather than with microorganisms (Chapter 3.0) as shown in Table 1. Regardless of how the life kingdoms are classified, the discussion of each chapter is approached in a similar manner and, assuming the data are available, is divided into sections called Metabolism and Effects. Metabolism (Metabolic Processes) in these reports, is used to describe the factors which ultimately determine the body burden and form of the pollutant in the organism. This section is discussed from the standpoint of uptake and absorption, transport and distribution, biotransformation and elimination.

The Effects portion of each chapter or section presents data derived from both acute and chronic studies. The aim is to present information which would help establish clearly-defined cause-effect and dose-response relationships. General and detailed information pertaining to general toxicity, teratogenicity, mutagenicity, lethality, carcinogenicity, and growth and development, is of interest and should be included in the Effects section(s) under the proper heading. Data should be taken from epidemiological, clinical, and experimental laboratory studies.

Where possible, the influence of other substances and life forms, disease states, drugs, habits (such as smoking or alcohol consumption), etc., on Metabolism and Effects should be considered. In the real world, the above conditions often exist and may be of importance. For example, it has been shown that calcium and iron deficiencies, diets, and hereditary enzyme deficiencies in children can affect lead absorption and toxicity (2-5). These factors must be considered if the health and ecological hazards of a pollutant are to be "accurately" assessed.

Sections 7.0 and 8.0--Environmental Sections

Localized in these two chapters which in some cases have been combined into one, is information relevant to mechanisms of environmental transport, transformation and interactions, movements through food chains and model ecosystems. Pollutant levels in various media, for what are thought to be situations representing both normal and abnormal levels, are also summarized here. As part of the above discussions, items of interest include media distribution processes and rates, and data on persistence and degradation in each of the media. The goal of these two chapters is to provide a link between the chemical and biological chapters 2-6, and the environmental chapters 7-8. Since the physical and chemical properties and biological aspects have been covered in detail in prior sections, the discussions on mechanisms and rates can be general but always supported by detail located in other sections. Figures which illustrate the flow of the hazardous pollutant through the environment, subsequent environmental and biological interactions, incorporation in food webs, and environmental sinks are included to support the discussion.

Before leaving the discussion of format and scope, it is important to point out a particular facet of this "modular" format which must be considered if the document is to be efficient and concise but still complete. In many cases information is relevant to more than one chapter or section. The potential for vast duplications and repetitions of the same information looms as a potential disadvantage. Recognizing this problem, contractors are encouraged to maintain close coordination among their writers so that each is aware of what information will be necessary in each section and what level of detail is required. Decisions can then be made as to the primary location of the information. It therefore becomes very important to have closely coordinated chapter to chapter and section to section referencing to direct the reader to pertinent information covered in greater or lesser detail in other parts of the document.

SOME GENERAL FINDINGS

Since this program is primarily concerned with the review of existing literature and is not a basic research program, outstanding or newsworthy findings were not anticipated. In that light, some of the general findings of the program to date will be presented.

Acute Data

Generally, a plethora of information relative to acute and subacute exposures of experimental animals, wild and domesticated animals, and humans is available. Much of what we know about metabolic processes and potential toxicities of these pollutants is indeed derived from acute data. Besides providing a means for studying mechanisms of toxicity, acute data may provide insight regarding the degree of hazard that might be associated with exposure to relatively high concentrations of the substance as well as an indication of those physiological systems or organs which may be affected.

Chronic Data

Although some chronic data on animals and humans are available, there are those that feel that "good" data on chronic exposures and "low levels" (similar to environmental levels) are lacking. This is especially true as it relates to assessing the carcinogenic potential of pollutants. As pointed out in a report to Congress, "even in the case of recognized carcinogens the actual risk posed by ingesting very low concentrations is not known at this time." (6)

Unfortunately, data are also incomplete regarding subtle changes in physiology, if any, that may occur as a result of exposure to environmental levels of pollutants. For example, in spite of a great deal of study, the debate over the role of cadmium as a potential etiological factor in hypertension still continues unresolved. The data at present are generally insufficient quantitatively and at times qualitatively to exactly predict the degree of hazard posed by levels of pollutants presently in or projected to be in our environment.

The picture is even cloudier since humans, animals, plants, etc., are often exposed to a combination of pollutants. We know little at this time about the effects (additive, protective, etc.) which may result from long-term simultaneous exposure to low levels of pollutants. Do different combinations and levels of pollutants in drinking water and air result in synergistic or antagonistic effects? This in only one of many questions which are unanswerable at this point in time and perhaps even in the future.

Placental Transfer

Most of the pollutants studied to date are capable of crossing the placenta. However, except in a few cases of exposure to relatively high concentrations of mercury (7-8) and PCB's (9), gross fetal effects have generally not been confirmed to be of environmental origin. Animal experiments have verified that pollutants will cross the placenta and in sufficiently high doses result in demonstrable teratological effects. Of more recent concern, however, are the possible occurrences of subtle fetal effects which may not be immediately apparent at birth but become manifest much later in postnatal development. For example, a recent retrospective study examining the effects of high concentrations of lead in drinking water (average about 400 micrograms/liter) suggests a strong correlation between lead levels in the drinking water and the development of mental retardation in children ages 2-6. The children studied were exposed to lead during gestation and early infancy. (10) Thus we can no longer be confident, if indeed we were, that failure to observe gross anatomical changes in newborns is proof of nonhazard.

Reactions in Waste Streams

The interactions and reactions of the hazardous materials are also of interest, particularly to those concerned with waste handling and disposal. The REEP documents provide basic information on physical and chemical properties which can be used to attempt to predict potential reactions, etc. However, the actual data on migration and chemical reactions of materials in complex waste streams are just being developed, some of which will be presented in part at this symposium. Unfortunately, most of the data will not be available soon enough to be incorporated into the REEP program.

Environmental Alterations of Pollutants

Finally, the form (speciation) of the pollutant in the environment, which is or can be an important determinant of its movement and potential toxicity, is at times not very clear. This is still the case with mercury. Although much research has been conducted and a good body of evidence indicates that inorganic mercury can be converted in water environments to the more toxic organic mercury, there are those who suggest that this transformation cannot occur sufficiently fast or quantitatively to be of environmental concern. (11) Similarly, recent evidence suggests that inorganic lead can be converted by microorganisms in lake sediments into volatile tetralkyl lead compounds. (12) To what extent this occurs in the environment, if at all, still needs to be defined.

In summary, documents such as the REEPs can be and remain (with constant updating) valuable sources of information to EPA and others.

TABLE 1. TOPICAL OUTLINE OF ENVIRONMENTAL EFFECTS REPORTS

1.0 Summary
  1.1 Summary of Findings
  1.2 Conclusions
2.0 Chemical and Physical Properties and Analysis
3.0 Biological Aspects in Microorganisms (generally unicellular forms but may include plankton)
  3.1 Bacteria
  3.2 Protozoa
4.0 Biological Aspects in Plants
  4.1 Non-Vascular (algae, fungi, mosses)
  4.2 Vascular
5.0 Biological Aspects in Wild and Domestic Animals
  5.1 Fish and Aquatic Organisms
  5.2 Birds and Terrestrial Wildlife
  5.3 Domestic Animals
  5.4 Etc.
6.0 Biological Aspects in Humans
7.0 Media Distribution and Processes
8.0 Environmental Interactions and Their Consequences

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HAZARDOUS WASTE SAMPLING

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ABSTRACT

Procedures and equipment for the sampling of liquid and sludge hazardous wastes will be discussed. The techniques are primarily applicable to bulk (vacuum trucks) and barreled wastes. Materials of a wide range of viscosity, corrosivity, volitivity, and solids content have been sucessfully handled. The techniques are designed to give representative samples of actual complex multiphase wastes. Equipment design is simple and inexpensive and allows for rapid sampling necessary for obtaining total input data on large hazardous waste sites. Sampling handling and preservation will be discussed in light of the wide variety of wastes handled. Appropriate sampling techniques do not necessarily produce samples statistically representative of the total waste stream. In our experience, the presence of sampling personnel significantly perturbs the flow of waste into a disposal site. Approaches to deal with this problem will be discussed. Our experiences in a large-scale sampling program in the Los Angeles area at six hazardous waste sites will be related as well as the approaches to classification and analysis of the resultant hazardous waste potpourri.

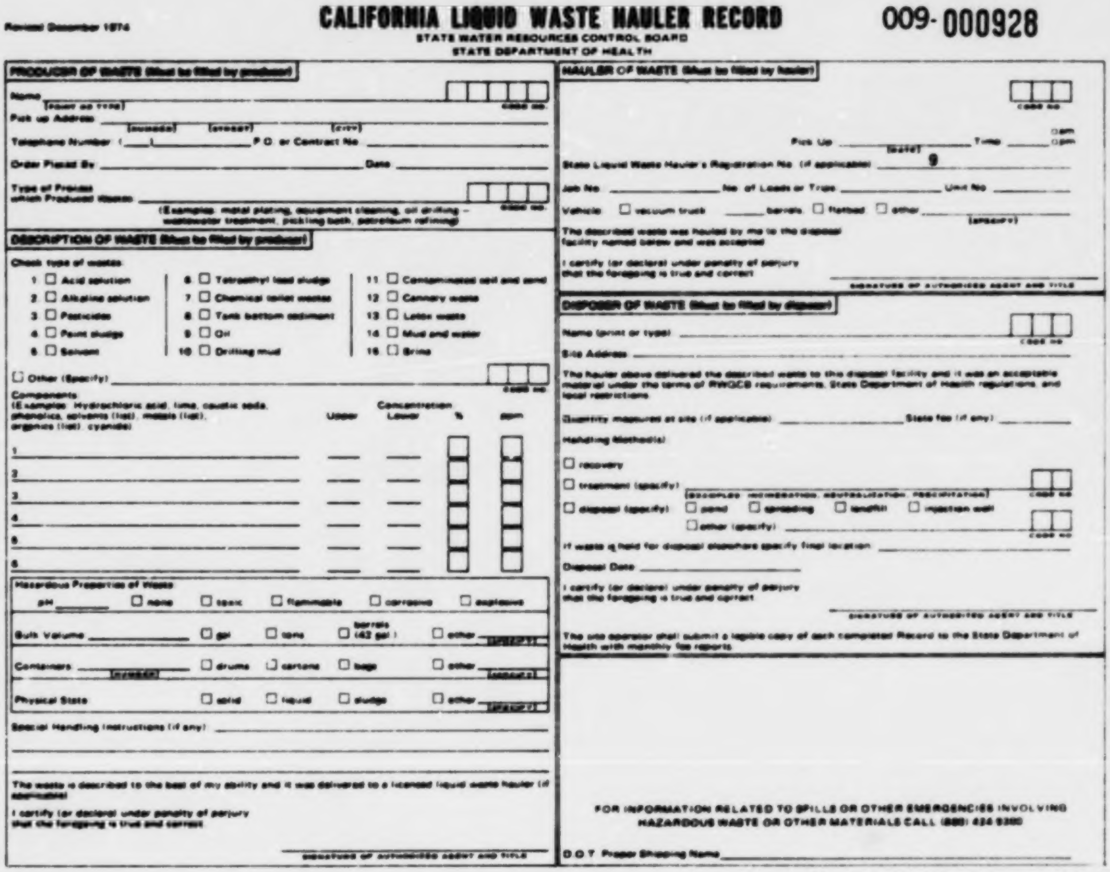
INTRODUCTION

The State of California, Department of Health has been involved in several aspects of sampling of hazardous wastes. These activities have necessitated the development of sampling equipment and procedures, as well as sample preservation and analytical procedures. In this development many problems of waste complexity, intractability and hazard have been encountered. We have determined, however, that successful sampling and analysis of hazardous wastes is vital to a management system.

TEXT

The California Department of Health is charged with the responsibility for setting up a statewide management program for hazardous waste. In this program we are concerned with many aspects of hazardous waste generation, transport, recovery, and disposal in terms of the environmental and public health impacts. One of the primary tasks which faced us in our program was to obtain information on the identity of hazardous wastes generated and disposed of in the State. Much information was available to us from a variety of industry studies, many of which were sponsored by the U.S. Environmental Protection Agency. Although these studies have been invaluable to our program, they were not fully adequate for our needs for two reasons. First, much of the information on the waste identity contained in these studies is based on estimates of both waste volumes and composition and not analytical data on actual wastes. Extrapolation of such estimated data to different areas of the county and to different industries was felt to be unsatisfactory. Second, except in a few cases, the information is not in sufficient detail to be of great assistance for disposal site or regional waste management.

It therefore became apparent that a certain amount of analytical data would have to be generated from samples taken from real hazardous wastes. This sampling and analysis program would be designed to complement a new State hazardous waste manifest system in which producers of hazardous waste are required to reveal the chemical identity and concentration of all hazardous waste components prior to shipment from production facility. A facsimilie of this new manifest is shown in Figure 1.



Revised December 1974

CALIFORNIA LIQUID WASTE HAULER RECORD

STATE WATER RESOURCES CONTROL BOARD
STATE DEPARTMENT OF HEALTH

009-000928

PRODUCER OF WASTE (Must be filled by producer)

Name ________ (print or type) ☐☐☐☐☐ code no.
Pick up Address ________ (number) (street) (city)
Telephone Number (___)________ P.O. or Contract No. ________
Order Placed By ________ Date ________
Type of Process which Produced Waste ________ ☐☐☐☐ code no.
(Examples: metal plating, equipment cleaning, oil drilling – wastewater treatment, pickling bath, petroleum refining)

DESCRIPTION OF WASTE (Must be filled by producer)

Check type of wastes:

1 ☐ Acid solution
2 ☐ Alkaline solution
3 ☐ Pesticides
4 ☐ Paint sludge
5 ☐ Solvent
6 ☐ Tetraethyl lead sludge
7 ☐ Chemical toilet wastes
8 ☐ Tank bottom sediment
9 ☐ Oil
10 ☐ Drilling mud
11 ☐ Contaminated soil and sand
12 ☐ Cannery waste
13 ☐ Latex waste
14 ☐ Mud and water
15 ☐ Brine

☐ Other (Specify) ________ ☐☐☐ code no.

Components (Examples: Hydrochloric acid, lime, caustic soda, phenolics, solvents (list), metals (list), organics (list), cyanide)	Concentration Upper	Lower	%	ppm
1			☐	☐
2			☐	☐
3			☐	☐
4			☐	☐
5			☐	☐
6			☐	☐

Hazardous Properties of Waste
pH ________ ☐ none ☐ toxic ☐ flammable ☐ corrosive ☐ explosive
Bulk Volume ________ ☐ gal ☐ tons ☐ barrels (42 gal) ☐ other ________ (specify)
Containers ________ (number) ☐ drums ☐ cartons ☐ bags ☐ other ________ (specify)
Physical State ☐ solid ☐ liquid ☐ sludge ☐ other ________ (specify)
Special Handling Instructions (if any) ________

The waste is described to the best of my ability and it was delivered to a licensed liquid waste hauler (if applicable)

I certify (or declare) under penalty of perjury that the foregoing is true and correct

________ SIGNATURE OF AUTHORIZED AGENT AND TITLE

HAULER OF WASTE (Must be filled by hauler)

☐☐☐ code no.
Pick Up ________ (date) Time ________ ○am ○pm
State Liquid Waste Hauler's Registration No. (if applicable) 9
Job No. ________ No. of Loads or Trips ________ Unit No. ________
Vehicle: ☐ vacuum truck ________ barrels ☐ flatbed ☐ other ________ (specify)

The described waste was hauled by me to the disposal facility named below and was accepted

I certify (or declare) under penalty of perjury that the foregoing is true and correct

________ SIGNATURE OF AUTHORIZED AGENT AND TITLE

DISPOSER OF WASTE (Must be filled by disposer)

Name (print or type) ________ ☐☐☐ code no.
Site Address ________

The hauler above delivered the described waste to the disposal facility and it was an acceptable material under the terms of RWQCB requirements, State Department of Health regulations, and local restrictions.

Quantity measured at site (if applicable) ________ State fee (if any) ________
Handling Method(s)
☐ recovery
☐ treatment (specify) ________ (examples: incineration, neutralization, precipitation) ☐☐ code no.
☐ disposal (specify) ☐ pond ☐ spreading ☐ landfill ☐ injection well
☐ other (specify) ________ ☐☐ code no.
If waste is held for disposal elsewhere specify final location ________
Disposal Date ________

I certify (or declare) under penalty of perjury that the foregoing is true and correct

________ SIGNATURE OF AUTHORIZED AGENT AND TITLE

The site operator shall submit a legible copy of each completed Record to the State Department of Health with monthly fee reports.

FOR INFORMATION RELATED TO SPILLS OR OTHER EMERGENCIES INVOLVING HAZARDOUS WASTE OR OTHER MATERIALS CALL (800) 424 9300

D.O.T. Proper Shipping Name ________

Figure 1. Hazardous waste manifest.

The identification in such detail of hazardous components is something which requires considerable effort on the part of the waste producer. In our experience such efforts are not taken unless there is some attempt at verification. This verification has taken the form of sample collection and analysis.

A second and equally important aspect of the California Hazardous Waste Program is the surveillance and enforcement of State regulations on what wastes are to be handled and how they are to be treated. Assessment of waste hazards, environmental impacts and compatibilities must be primarily based on a sound knowledge of waste chemical composition. Such knowledge requires a simple, rapid, and representative sampling method along with good analytical techniques which provide the proper data.

Some of the parameters are listed below which must be considered in hazardous waste sampling programs.

Phase Complexity

Hazardous wastes appear as all phases: solid, aqueous, and organic liquid. Very often the waste is a complex mixture of all of these phases. Sampling techniques must be able to give representative fractions of all phases.

Access to Waste

Hazardous wastes are contained in ponds, vacuum trucks, barrels, etc. Sampling must be adaptable to all of these.

Chemical Reactivity

Many wastes are highly corrosive or strong oxidizers. Many wastes, although not particularly reactive, are, because of their physical nature, very hard on equipment. These features place severe demands on equipment design.

Safety

The relative undefined nature of most waste, creates a significant safety problem to sampling personnel. Rather extensive precautions must be taken.

Sample Containment and Preservation

The containment and preservation of corrosive, highly toxic, or highly volatile samples in the field, present significant problems.

The California Department of Health has been involved in two specific programs of hazardous waste sampling during this last six months. In cooperation with the University of Southern California, Environmental Engineering Department, under the direction of Dr. Kenny Chen, we have been involved in a "Case Study" of a major hazardous waste disposal site in southern California.

The location chosen for the study was the B.K.K. disposal site, located in the southern portion of the city of West Covina, in the San Jose Hills area. This site is classified by the State Water Resources Control Board as a "Class I" landfill. Under this classification, the site, or certain portions of it, possesses no continuity with ground waters or surface waters. With this classification, the site is virtually unlimited as to the type of waste which can be accepted. The primary exception is radioactive waste. The B.K.K. Company is one of the largest industrial waste disposal companies in the Western United States. It averages about $5x10^6$ gal./month of liquid waste. Approximately 60% of this volume is classified by the Department of Health as "hazardous". This volume represents approximately 30% of the liquid industrial waste "legitimately" disposed in the Los Angeles area and approximately 45% of the hazardous wastes. At the B.K.K. disposal site, extensive "total input" sampling was conducted over a period of two weeks. During this period several hundred samples were obtained which represented essentially all of the waste types taken at the site. Samples were taken with the sampler shown in Figure 2.

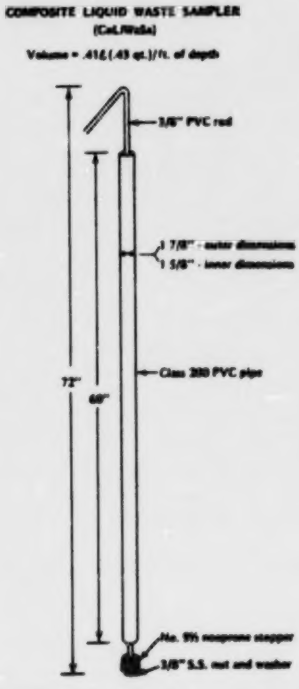

COMPOSITE LIQUID WASTE SAMPLER
(CoLiWaSa)
Volume = .41ℓ (.43 qt.)/ft. of depth
3/8" PVC rod
1 7/8" - outer dimensions
1 5/8" - inner dimensions
Class 200 PVC pipe
72"
60"
No. 9½ neoprene stopper
3/8" S.S. nut and washer

Figure 2. Composite Liquid Waste Sampler

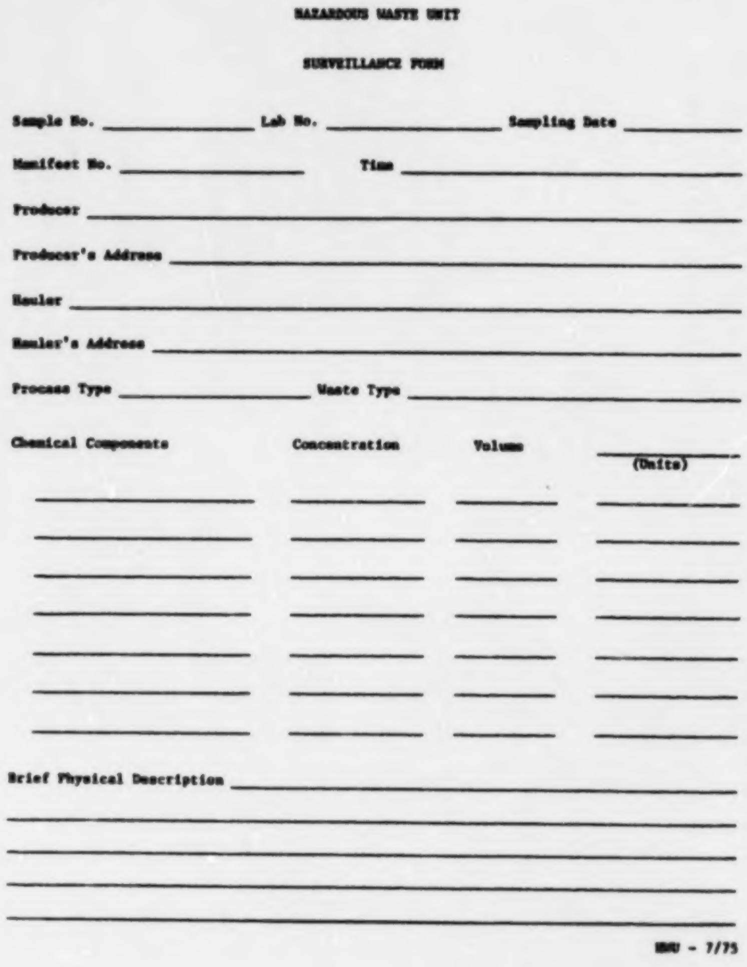
This device is relatively simple, consisting of a hollow PVC tube, nominally 1 1/2 inches I.D., with a concentric PVC rod which is attached to a neoprene stopper. The sampler is lowered into a liquid or sludge waste to cut across a column of material. The sampler is then closed at the bottom, trapping a sample inside which is representative of all the layers and phases of the waste. Volume of sample taken is about 350 ml/foot of depth of sample. Characteristics considered important in this sampling device are: It can be used on ponded, bulk, or containerized waste; sampling is rapid and simple; equipment can be readily cleaned; equipment is inexpenisve.

These characteristics are particularly important for a total input type sampling program at major disposal sites because of the large numbers of waste loads which must be sampled. Waste samples can be transferred directly from the sample tube to a sample container. The currently used polyethylene sample bottles are sealed immediately and stored in the field vehicle until the end of the day. At this time they are transported to cold storage (4°C), where they are kept until analysis begins. We attempt to start analysis within one week subsequent to sampling. We currently have no data relating to either the stability or instability of these samples after sampling. Proper and safe sampling procedures have been greatly aided by the new haulers manifest shown in Figure 1. This document usually gives a good indication as to the potential problems and safety hazards which may be encountered. Current usage of the waste hauler manifest gives fairly good information on general waste categories. Some of these categories are acids, alkalis, cyanides, pesticides, plating solutions, etc. Although this information is inadequate for the development of a chemical inventory of wastes, it is very helpful in the determinations of proper sampling procedures and in initial analytical techniques.

When the goal of a sampling program is to develop a chemical inventory of waste traffic at a disposal site, one must consider the effect of the sampling program on the flow of wastes. It has been our experience that the presence of sampling personnel at a disposal site significantly affects waste volumes. Information as to where sampling is being conducted rapidly spreads among haulers and disposal sites. This factor can lead to a totally unrepresentative sample of waste input. Our solution to this problem is to simultaneously sample all or most of the sites within a region. This eliminates the alternative, non-sampled, disposal site to the apprehensive waste hauler or site operator. This approach can however, be only partially successful because waste can be sorted, dumped at off hours, or illegally dumped. Some estimation of the perturbation caused by sampling can be estimated by an inspection of detailed records over a several month period. This is now possible in our department because of the waste hauler manifest and the automated data system which it supplies. Inspections are made of waste traffic into the sites in the region of a sampling program several weeks before and after the actual sampling. In this way any unusual fluctuations can be noted. This effect on waste volumes appears not to be a significant problem on spot checking or surveillance activities. In this type of operation, sampling personnel come and go on an irregular schedule, which precludes adaptation by the haulers and disposal sites.

Record keeping is of importance in any sampling program. In hazardous waste sampling, this becomes an important consideration when ten vacuum trucks are lined up at a disposal site, waiting to unload. To facilitate the process, the form shown in Figure 3. was used. This form is both sample record form and an analytical approach which is described on the reverse side.

Analysis of these waste samples pose some rather unique problems. The variety and complexity of them is sometimes overwhelming. In light of this, a workable scheme for the analysis had to be developed. Our approach has been to develop four levels or hierarchies of analytical complexity. At level I, only phase composition data is acquired, i.e. solid, aqueous, and organic liquid phases. Progressing through levels II, III, and IV, more and more detailed information is acquired about the waste composition. Level IV, is specific compound or ion analysis. The analytical flow scheme is shown on Figure 4. Decision on what initial analysis to do is usually based upon waste origin and composition information taken off the waste haulers manifest. More detailed analysis is usually



HAZARDOUS WASTE UNIT

SURVEILLANCE FORM

Sample No. ________ Lab No. ________ Sampling Date ________

Manifest No. ________ Time ________

Producer ________

Producer's Address ________

Hauler ________

Hauler's Address ________

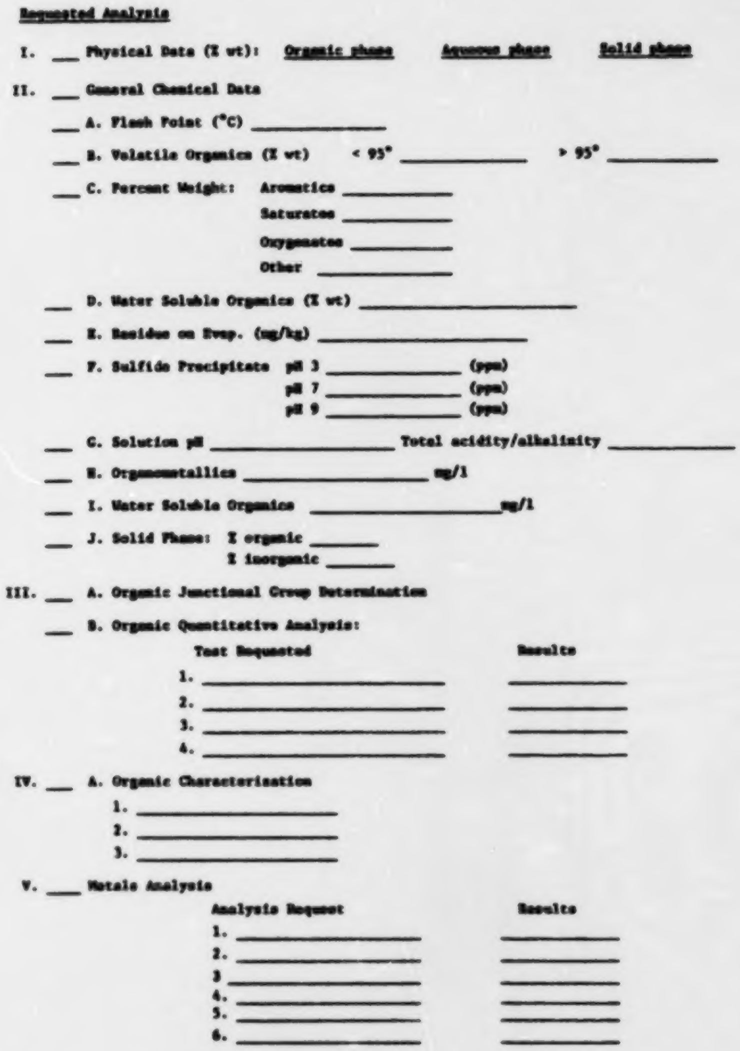
Process Type ________ Waste Type ________

Chemical Components	Concentration	Volume	________ (Units)
________	________	________	________
________	________	________	________
________	________	________	________
________	________	________	________
________	________	________	________
________	________	________	________
________	________	________	________

Brief Physical Description ________

HWU - 7/75

Figure 3a. California Liquid Waste Surveillance form.



Requested Analysis

I. ___ Physical Data (% wt): Organic phase Aqueous phase Solid phase

II. ___ General Chemical Data

___ A. Flash Point (°C) ________

___ B. Volatile Organics (% wt) < 95° ________ > 95° ________

___ C. Percent Weight: Aromatics ________
Saturates ________
Oxygenates ________
Other ________

___ D. Water Soluble Organics (% wt) ________

___ E. Residue on Evap. (mg/kg) ________

___ F. Sulfide Precipitate pH 3 ________ (ppm)
pH 7 ________ (ppm)
pH 9 ________ (ppm)

___ G. Solution pH ________ Total acidity/alkalinity ________

___ H. Organometallics ________ mg/l

___ I. Water Soluble Organics ________ mg/l

___ J. Solid Phase: % organic ________
% inorganic ________

III. ___ A. Organic Junctional Group Determination

___ B. Organic Quantitative Analysis:

Test Requested	Results
1. ________	________
2. ________	________
3. ________	________
4. ________	________

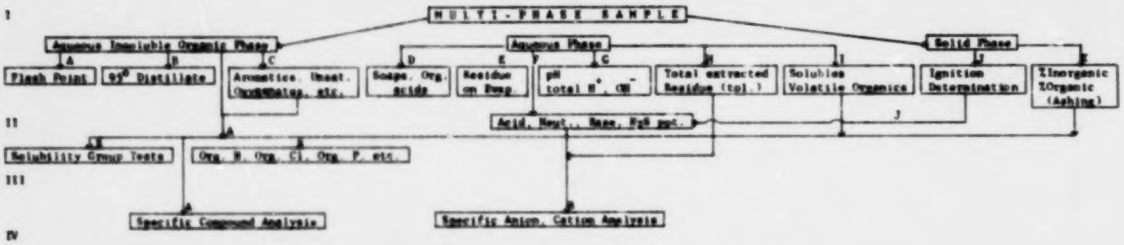
IV. ___ A. Organic Characterization

1. ________
2. ________
3. ________

V. ___ Metals Analysis

Analysis Request	Results
1. ________	________
2. ________	________
3 ________	________
4. ________	________
5. ________	________
6. ________	________

Figure 3b. Hazardous Waste Analysis Form (reverse side of surveillance form).


I
MULTI-PHASE SAMPLE
Aqueous Immiscible Organic Phase
Aqueous Phase
Solid Phase
A
B
C
D
E
F
G
H
I
J
K
Flash Point
95° Distillate
Aromatics, Unsat. Oxygenates, etc.
Soaps, Org. acids
Residue on Evap.
pH total H+, OH-
Total extracted Residue (tol.)
Solubles Volatile Organics
Ignition Determination
%Inorganic %Organic (Ashing)
II
Acid, Neut., Base, H2S ppt.
J
A
B
Solubility Group Tests
Org. N, Org. Cl, Org. P, etc.
III
A
B
Specific Compound Analysis
Specific Anion, Cation Analysis
IV

EXPLANATION OF STEPS

I Sample separation: Sample is separated into respective phases. In case of emulsions or sludges, use appropriate separation techniques - Record % weight and % volume of Aqueous, Organic, and Solid phases (Dry weight).

II A. Flash point determination on organic liquid.
B. Volatile organic determination done on all samples with organic phase: 10% by volume, record weight % <95° B.P. and >95° B.P.
C. Separation using appropriate technique to separate class of organic cpds. i.e. aromatics, saturates, alcohols etc. Record % weight of each class.
D. Acidify aqueous phase and extract with freon. Evaporate solvent and record % weight extractable, non volatile organics.
E. Evaporate aqueous layer to dryness and record residue or evaporation. Subtract organic extractables from total residue.
F. Precipitate metals as sulfide in acid, neutral, and base solution.
G. Record pH titrate for total alkalinity/acidity.
H. Toluene extract of Aqueous layer. Evaporate toluene, ash residue, record residue for organometalics.
I. Steam strip and record weight of volatile, water soluble organics.
J. Ignite solid - determine general organic, inorganic nature.
K. If solid is mixture, dry at 105°, then ignite, record % organic and inorganic.

III A. Do standard solubility tests for organic functional groups (qualitative) - Record all positive and negative tests.
B. Organic nitrogen, sulfur, chlorine, phosphorus, quantitative tests as requested. Do standard qualitative scheme for anion and cation groups.

IV A. Specific identification of organic molecules with appropriate technique. Record identity and % weight of each cpd. found.
B. Specific quantitative cation, anion analysis (quant.) by appropriate technique as requested.

Figure 4. Flow scheme for waste analysis.

done on the basis of indications from the preliminary data. Using this approach we are able to develop general analytical data on all samples taken and to concentrate efforts on selected samples for detailed analysis. The analytical program is currently nearing completion of the work on samples taken in the "total input" study. I am, however, not as yet prepared to discuss these results in detail. A report will issue jointly from the Environmental Engineering Department at U.S.C., and the California Department of Health, later in the spring, covering this data.

The methods used in analysis in general have been classical wet chemical methods including centrifugation, steam distillation, gas chromatography and others. Metals analysis has been by digestion and atomic absorption on a selected group of 20 metals. In addition we are working on a rapid elemental scanning technique using X-ray fluorescence. This method will allow simultaneous determination of 50-60 elements with a minimum of sample preparation. In fact, many samples may be analyzed directly after a simple homogenization.

Our current effort is directed toward the development of well standardized procedures for waste sampling and the incorporation of these procedures in a field manual which will be suitable for use by regulatory agencies, waste generators, haulers, and disposal sites. We also are attempting to develop a standard scheme for "waste to standard methods" suitable for publication in manual form.

Now, as California begins a new stage of hazardous waste regulation, with full-time field inspection, surveillance and sampling, the methods that have been developed will be put to severe test. The next six months will determine whether they will withstand the test.

The author would like to fully acknowledge the valuable assistance of the many co-workers at the U.S.C. Environmental Engineering Department and the California Department of Health, as well as the financial assistance of the U.S. Environmental Protection Agency.

THE EFFECTS OF THE DISPOSAL OF INDUSTRIAL WASTE WITHIN A SANITARY LANDFILL ENVIRONMENT

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ABSTRACT

In an effort to assess the impact of the practice of co-disposal of industrial waste materials with municipal refuse, a project utilizing 3 ton experimental landfill test cells was undertaken. Concern has been voiced that the addition of industrial wastes may result in the occurrence of various toxic elements in leachates and thereby pose a potential threat to potable groundwater supplies.

A combination of municipal solid waste and various solid and semi-solid industrial and municipal wastes were added to several test cells. All material flows were accurately measured and characterized, for the continuing study. Data are presented on the chemical and microbial composition of the leachates and the gases produced.

INTRODUCTION

Environmental effects from landfilling result from not only soluble and slightly soluble materials disposed of in the landfill but also from the products of chemical and microbial transformations. These transformations should be a consideration in management of a landfill to the extent that they can be predicted or influenced by disposal operations. The motivational aspects of this project were the lack of quantitative data on the decomposition processes under field conditions and, in particular, the introduction of solid and semi-solid industrial waste.

APPROACH

In an effort to evaluate the effects of the co-disposal of industrial wastes materials with municipal solid waste, nineteen (19) large scale experimental test cells, Figure 1, are being monitored to achieve the following objectives:

1. Assess varying rainfall regimens, 203.2 to 812.8 mm/yr (8.0 to 32.0 inches per year), on the rate of decomposition and the resulting mass flow of gases and leachates (cells 1-4).

2. Determine the impact of municipal sewage sludge additions on the rates of decomposition and gas and leachate.

3. Determine the impact on decomposition rates by the addition of a pH buffer (limestone) into the waste during landfill construction (cell 8).

4. Determine the survival of polio virus in a landfill environment (cell 15).

5. Determine if differences in ambient soil temperatures significantly affect the rate of decomposition in gas and leachate production (cells 2 and 16).

6. Determine the impact on decomposition in gas and leachate production of the co-disposal of six selected industrial residuals with municipal solid waste (cells 9, 10, 12, 13, 14, and 17).

7. Determine the ability of duplicate test cells to generate similar physical and analytical data (cells 18 and 19).

8. Determine the impact on decomposition rates in gas and leachate production by rapidly bringing the municipal solid wastes to field capacity (cell 11).

The test cells (experimental landfills), employed for this study were epoxy coated steel, 1.8 meter (6 ft.) in diameter and 3.6 meters (12 ft.) in height; capable of holding approximately 3000 kilograms (6600 lbs.) of municipal solid waste in a manner comparable to large area landfills. The size of the test cells was selected to minimize problems of scaling factors generally associated with smaller laboratory lysimeters and to avoid the use of shredded refuse. Larger test cells would have been more costly to construct and provide adequate instrumentation. A total of fifteen (15) cells were placed in the ground outdoors with the remaining four (4) cells in an enclosed bay area where higher ambient temperatures were maintained. Five (5) of the industrial waste test cells (cells 9, 10, 12, 13, and 14) were located outside and one (cell 17) industrial waste cell inside. Prior to placement of any solid and/or industrial waste, a layer of silica gravel, 300 mm deep, was placed in all cells as a base for the solid waste and to allow leachate to permeate to the drain system. Laboratory studies of the silica gravel showed it to be non-reactive to leachate. All test cells were coated with coal tar based epoxy which was proven to be resistant to leachate.

All test cells were loaded simultaneously in a period of five (5) days employing the loading sequence outlined below.

Municipal solid waste from the City of Cincinnati was obtained directly from the packer truck and deposited on a concrete mixing pad. All trash bags were hand slit and mixing was accomplished employing a front end loader. A truck with a removable bed was utilized to deliver an 18.2 kg (40 lb.) characterization sample and an 11.4 kg (25 lb.) chemical, microbiological, and moisture sample for subsequent analysis for each 363 kg (800 lb.) increment of waste delivered to each test cell. As solid waste was being added to the test cells, the industrial or municipal sludge wastes were added simultaneously. After each increment of waste was added, the solid waste or the solid waste and sludge was mixed manually. Each increment of solid waste was compacted to a height of 300 mm (1 ft.) and a density of 470 kg/cu.m (800 lb/cu.yd.) using a 21m (70 ft.) crane with a 1318 kg (2900 lb.) drop weight. This sequence was repeated 8 times for each test cell to provide 2.4 m (8 feet) or approximately 3000 kilograms (6600 lb.) of compacted solid waste.

The solid waste was then covered with 300 mm (1 ft.) of compacted clay and all cells were shielded from both moisture and sunlight. Temperature monitors are installed throughout all cells and in the soil at various locations within the

CELL NO	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	
WASTE STREAM	—	—	—	—	SEWAGE SLUDGE	SEWAGE SLUDGE	SEWAGE SLUDGE	[illegible]	PETROLEUM SLUDGE	BATTERY WASTE	[illegible]	ELECTROPLATING WASTE	[illegible] WASTE	CHLORINE PROD. BRINE SLUDGE	[illegible]	—	SOLVENT BASED PAINT SLUDGE	—	—	
AMT [illegible]					[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			[illegible]			
TOP TYPE *	OPEN CLOSED	OPEN CLOSED	SEALED	SEALED	OPEN CLOSED	OPEN CLOSED	OPEN CLOSED	OPEN CLOSED	OPEN	OPEN	OPEN [illegible]	OPEN	OPEN	OPEN	OPEN CLOSED	SEALED	SEALED	SEALED	SEALED	
ANNUAL MOISTURE [illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	4064	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
TEMP PROBES	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	6	6	6	6	6	
GAS PROBES	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
TOTAL MASS SOLID WASTE	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	

[illegible]

[illegible]

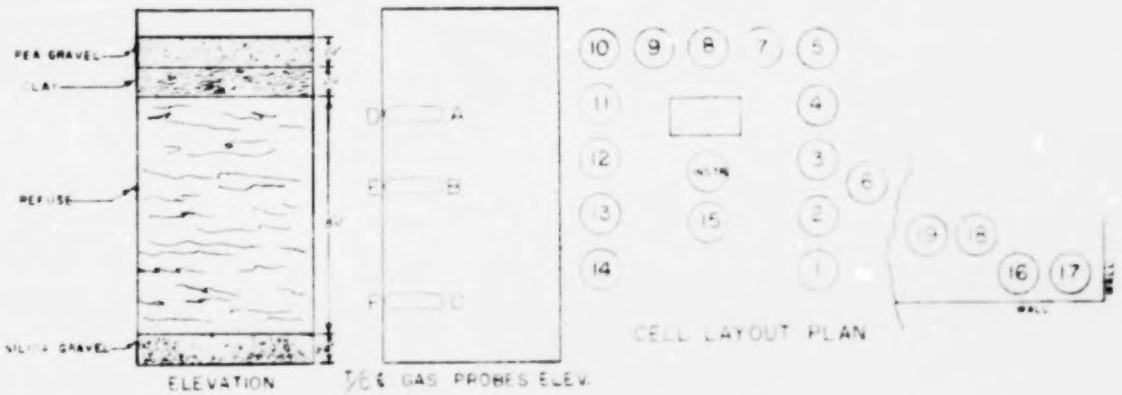
PEA GRAVEL
CLAY
REFUSE
SILICA GRAVEL
ELEVATION
D
A
E
B
F
C
GAS PROBES ELEV.
10
9
8
7
5
11
4
12
INSTR
3
6
13
15
2
19
18
14
1
16
17
WALL
WALL
CELL LAYOUT PLAN

FIGURE 1. OPERATIONAL CHARACTERISTICS OF EXPERIMENTAL LANDFILLS.

solid waste. This solid waste was hand separated into nominal categories (paper, glass, food wastes, etc.) and chemical and microbiological analyses were performed on the individual categories and on composite samples. Water addition to the cells at a rate of 406 mm (16 inches) per year is accomplished on a monthly basis in accordance with anticipated net infiltration for the midwestern portion of the country.

INDUSTRIAL RESIDUALS UNDER STUDY

The industrial process residuals evaluated included a refinery sludge (RS), battery production waste (BPW), an electroplating waste sludge(EW), an inorganic pigment sludge (IPW), a chlorine production brine sludge (CPBS), and a solvent based paint sludge (SBPS). The physical characteristics and amounts of industrial wastes added to each cell are provided in Table 1.

The refinery sludge is a by-product of the refining of crude oil. The waste material obtained is what is termed API bottoms sludge. This is a material resulting from a gravity oil/water separator which is very high in biological activity.

The battery production waste was obtained from the manufacturer of lead/acid storage batteries. The waste is a composite from all phases of a manufacturing operation with the exclusion of the battery plate assembly section itself. This operation is a closed system from which the waste material is shipped to a smelter for the recovery of lead. The waste obtained goes through a neutralization process before entering a settling pond from which the sludge was obtained.

The electroplating waste was obtained from a large plating firm which employs the following plating processes: Chromium (Cr), Nickel (Ni), Cadmium (Cd), Copper (Cu), Iron (Fe) and Zinc (Zn). No tin plating occurs at this firm. These wastes were treated in various categories. The chromium wastes were converted to trivalent chromium (Cr + 3) by the addition of sulfur dioxide in an acid system (pH 3.0). The pH was then raised to approximately 8.0 with caustic to precipitate the trivalent chromium. The cyanide containing wastes were treated by raising the pH of the water with caustic and then breaking down the cyanogen systems by the addition of sodium hypochlorite. All other acid wastewaters were treated with base to elevate the pH to a range of 8 to 9. The wastewaters were then pumped to a lagoon for settling. The sludge used was a brown soupy material which contained large amounts of liquids.

Inorganic pigment waste was from a supplier whose main product was titanium dioxide. It was obtained by processing raw ore through numerous production stages. Wastewaters from the various manufacturing operations were pumped to a single facility and treated simultaneously. The water was pumped to a primary settler during which the pH was raised with base and an alkaline precipitate forms. This sludge was then dewatered and the residue removed. The waste used was a black solid material containing very little moisture.

The chlorine production brine sludge was obtained from a manufacturer employing the mercury cell technique for chlorine liberation. In this facility, the production of chlorine was by the electrolysis of sodium chloride in a mercury cell. As the electrolysis proceeded, chlorine was liberated at one electrode while a sodium/mercury amalgam was formed at the other. The majority of the sludge (60 to 80%) was from the brine saturator while the remainder was from the clarifier after settling. The sludge used appeared somewhat moist, brown in color, and extremely dense.

TABLE 1. INDUSTRIAL WASTE PHYSICAL CHARACTERISTICS

Cell	Waste Type	Moisture[a] Content	Amount Added[b]	Characteristics
9	RS[c]	79.00	1518	High bacterial activity, black moist
10	BPW[d]	89.25	1291	Grey-lg amount of liquid
12	EW[e]	79.53	1191	Brown, soupy
13	IPW[f]	51.75	1420	Black, solid, no odor
14	CPBS[g]	24.11	2039	Very dense, no odor, light brown, moist
17	SBPS[h]	24.75[i]	1604	Red to white color, putty consistency, strong odor

[a] Percent by wet weight.

[b] kg.

[c] Refinery Sludge.

[d] Battery Production Waste.

[e] Electroplating Waste.

[f] Inorganic Pigment Waste.

[g] Chlorine Production Brine Sludge.

[h] Solvent Based Paint Sludge.

[i] Mainly organic solvents.

The solvent based paint sludge used was representative of a paint sludge produced in industries involved in painting large numbers of metal products. Paint overspray was caught in a water curtain and was pumped directly to a holding tank for disposal with no pretreatment. The material was very high in organic solvents and was extremely viscous, its color dependent upon the pigments present.

The chemical analyses of these waste materials, Table 2, indicated that the sludges contained toxic materials; their leachability, still was not known.

Notable components of these sludges were: Cu, Fe, Hg and moisture for the refinery sludge; Cu, Fe, Cd, Pb, asbestos; Sn, Sb and moisture for the battery production waste; Cr, Fe, As, Cd, cyanide and moisture for the electroplating wastes; Be, chloride, asbestos, clay volatile fibers and moisture in the inorganic pigment waste; and Ni, Pb, chloride, asbestos, Hg and clay volatile fibers for the chlorine production brine sludge.

LEACHATE AND GAS MONITORING

All leachates are collected anaerobically (under an argon stream) from a centrally located observation cell. Gaseous samples are collected via gas lines leading to an instrumentation shed. Gas composition is determined by gas chromatography. All leachates are collected on a bimonthly basis and gas samples are taken on a monthly basis.

Leachate Composition

Immediately after compaction, small volumes (less than 1 liter) of leachate were obtained from the majority of the cells. Chemical analyses of the leachate indicated high concentrations of metals present; organic analyses of these same liquids indicated very small amounts of carbon containing material present. Based on these chemical characteristics and the time of appearance, it was concluded that these initial volumes of liquid were interstitial water squeezed from the refuse, or refuse/sludge mixture as a result of the compactive effort and was not truly leachate derived from infiltrating water and decomposition processes. After collecting the initial squeezings from the test cells, no further liquid was produced for a period of approximately six months. At this time leachate production was noted. The occurrence of leachate was attributable to several factors. First, the number of available moisture retention sites was reduced by the addition of the high moisture content industrial wastes, i.e., the refining wastes, chlorine production brine sludge, etc. For this reason, field capacity was approached at a much earlier date than originally expected. Data indicate that field capacity was reached in cell 14 and was rapidly being approached in cells 12 and 13. Secondly, it appeared there was channeling within the solid waste/industrial waste test cells. Channeling prolongs the time required to reach field capacity, but allows the early appearance of leachate.

The organic acid concentration histories in leachates from refuse/CPBS, refuse/IPW, refuse/EW and refuse alone were similar, though not identical; peak concentrations occurred between the 8th and 11th months; Figures 2. Of these leachchates, that from the refuse/CPBS had the lowest peak concentration, i.e., approximately 61 percent of the refuse peak. Leachates from the refuse/EW and refuse/IPW had peaks which were 38 percent greater and 29 percent greater respectively than the refuse leachate. The short term data compiled does not permit determination of the significance of these differences in peak organic acid concentrations.

TABLE 2. INDUSTRIAL WASTE CHEMICAL ANALYSIS[a]

Waste Cell Number	RS[b] 9	BPW[c] 10	EW[d] 12	IPW[e] 13	CPBS[f] 14	SBPS[g] 17
Total Solids[h]	21.00	10.75	20.47	48.25	75.89	75.25
Total Volatile Solids[h]	31.00	7.94	8.98	22.25	1.17	55.31
Moisture[h]	79.00	89.25	79.53	51.75	24.11	24.75
Cr	125	155	1.56[h]	0.50	5.00	75.0
Ni	23	32	35	10	65	0.5
Cu	3500[i]	1125	100	110	125	2.0
Fe	5560	2950	1.37[h]	1000	2000	150
As	1.0	72	460	3.4	14.5	12.8
Be	4.8	1.8	0.25	20.2	<1.0	<1.0
Se	26.0	180	4.50	16.0	16.5	7.60
Cd	0.50	29.0	38.5	10.5	0.70	0.50
Cn	1.0	4.2	460	3.4	14.5	12.8
Pb	182	3.48[h]	267	120	697	12.6
Cl[h]	2.35	1.12	1.35	10.0	20.0	0.75
Asbestos[j]	3.00	208	23.0	45.0	110	9.00
Hg	10.6	4.80	14.7	7.60	227	16.7
Sn	NA[k]	6800	NA	NA	NA	NA
Sb	NA	1.32[h]	NA	NA	NA	NA
Clay Volatile Fibers[j]	40.0	720	86.0	185	480	65.0
Zn						
V	NA	120	NA	40	NA	NA
B	7.20	8.10	19.0	28.5	1.70	11.4
Ti	NA	NA	NA	NA	<0.1	NA

[a] All values in ppm unless otherwise specified.

[b] Refinery Sludge.

[c] Battery Production Waste.

[d] Electroplating Waste.

[e] Inorganic Pigment Waste.

[f] Chlorine Production Brine Sludge.

[g] Solvent Based Paint Sludge.

[h] Percent by wet weight.

[i] Underlined values indicate maximum sludge concentrations.

[j] Fibers/100 g.

[k] Not analyzed.

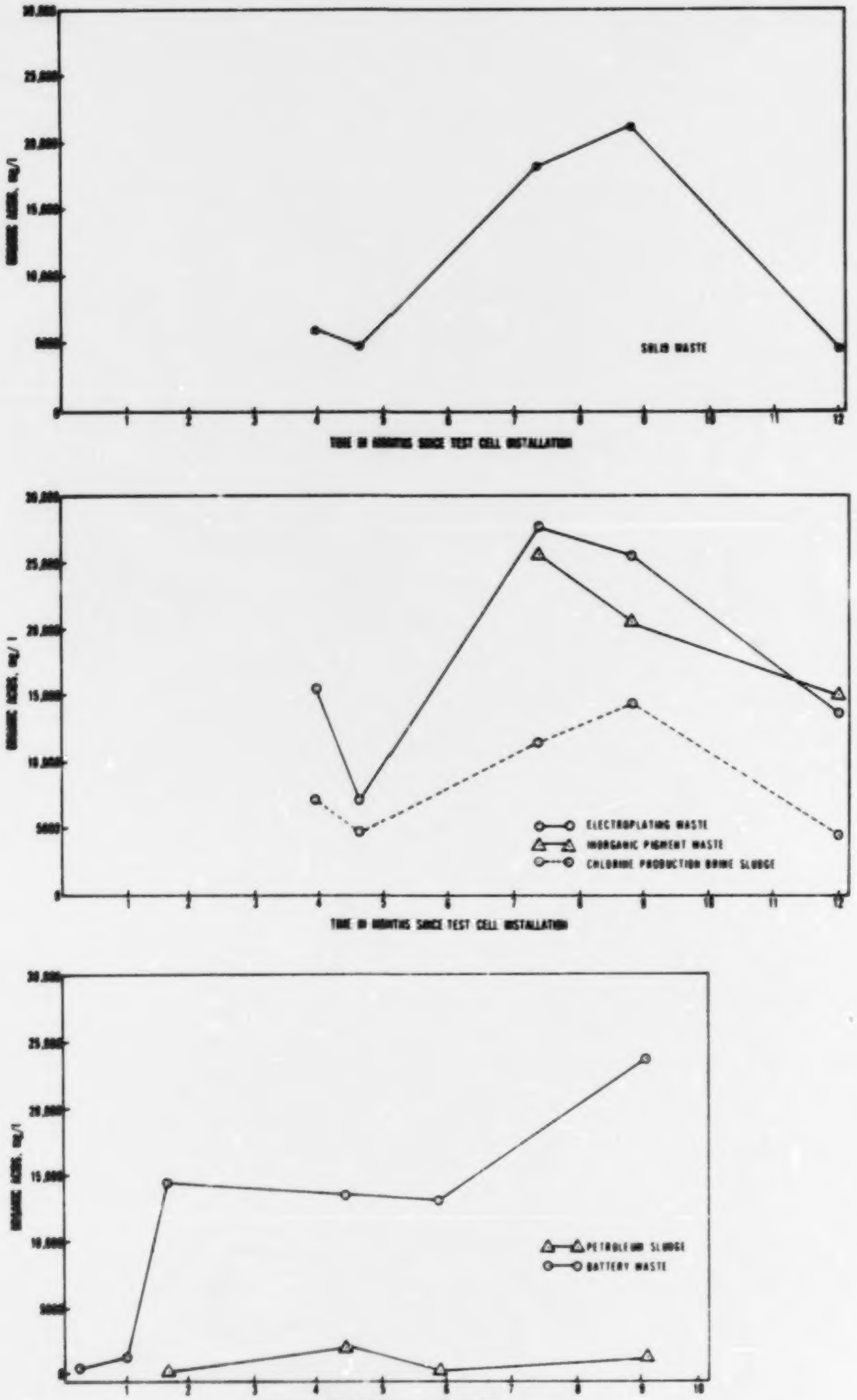

FIGURE 2. TOTAL ORGANIC ACIDS IN LEACHATE

The organic acid concentration data for both the refuse/BPW and refuse/RS failed to display any peaks. The graphical display of the refuse/BPW data, Figure 2, is indicative of microbial inhibition within this cell. Gas analysis has failed to indicate any vigorous methane production while COD and TOC data verified the low organic acid content of this leachate. The refuse/RS organic acid concentration history, Figure 2, indicates extremely vigorous decomposition occurring which has kept the quantity of organic acids low. Gas composition data has shown conversion from aerobic to methanogenic within several months of solid waste placement.

The total organic carbon (TOC) histories for leachates emanating from the refuse/CPBS, refuse IPW, refuse/EW and refuse alone, Figure 3, were again quite similar. Peaks occurred between the 5th and 7th months and again between the 9th and 10th months. The decline noted between the 7th and 9th month was caused by the lack of moisture entering the test cells during that time period. The refuse/BPW and refuse/RS, Figure 3, showed low concentrations of TOC for the reasons alluded to earlier.

Concentration histories for chemical oxygen demand (COD) in the leachates of refuse/CPBS, refuse/IPW, refuse/EW and refuse alone were again very similar. Increasing concentrations were noted as the decomposition proceeded with a greater rate of increase during periods of water infiltration. The concentration history of the refuse/BPW behaved in a similar manner but at a reduced level due to bacterial inhibition. The refuse/RS indicated low COD concentrations because of the rapid digestion taking place.

Anaerobic production of organic acids at a rate greater than their assimilation by other organisms, or greater than the indigenous buffering system causes the pH to range from 4 to 6. This acidic, reducing condition generally increases the solubility of cations such as Cd, Figure 4 and Fe Figure 5.

The Cd concentrations in leachates from the refuse/IPW and the refuse/CPBS climbed rapidly to 0.8 and 0.5 mg/l, respectively after leachate production began. The Cd concentrations from the refuse/CPBS continued to increase, ultimately to 1.2 mg/l, but at a slower rate. In contrast, leachate from the refuse only showed a comparable rapid increase of Cd to a peak of 0.5 mg/l when leachate modulation began, but then rapidly decreased to a relatively constant emission of 0.14 mg/l. This decrease may be indicative of the removal of readily soluble Cd followed by a lower, but steady release of less available Cd. The limited data available for Cd in leachates from the refuse/RS and refuse/BPW has not shown such a peak, possibly due to their later installation, and consequently the smaller quantity of water added to these test cells. The refuse/EW leachate Cd concentrations also did not show the rapid increase noted earlier; possibly due to availability of the Cd. The significance of the Cd data are two-fold: all Cd may not be equally available in the different waste streams and where Cd was readily available, in CPBS and IPW, the leachate Cd concentration remained 4 to 10 times greater than for refuse only.

The influence of the reducing conditions on cation concentration was exemplified by Fe, Figure 5. There was similarity in the concentration histories for all leachates except for those from the refuse/CPBS. The refuse/IPW ranged from 9 to 25 percent greater and the refuse/BPW ranged 16 to 25 percent less than the iron in leachate from refuse alone. The refuse/CPBS derived leachates never exceeded 90 mg/l or 28 percent of the iron combined in the refuse. The high chloride content, 20 percent, of the CPBS was suspected to be important in these results, but a relatively

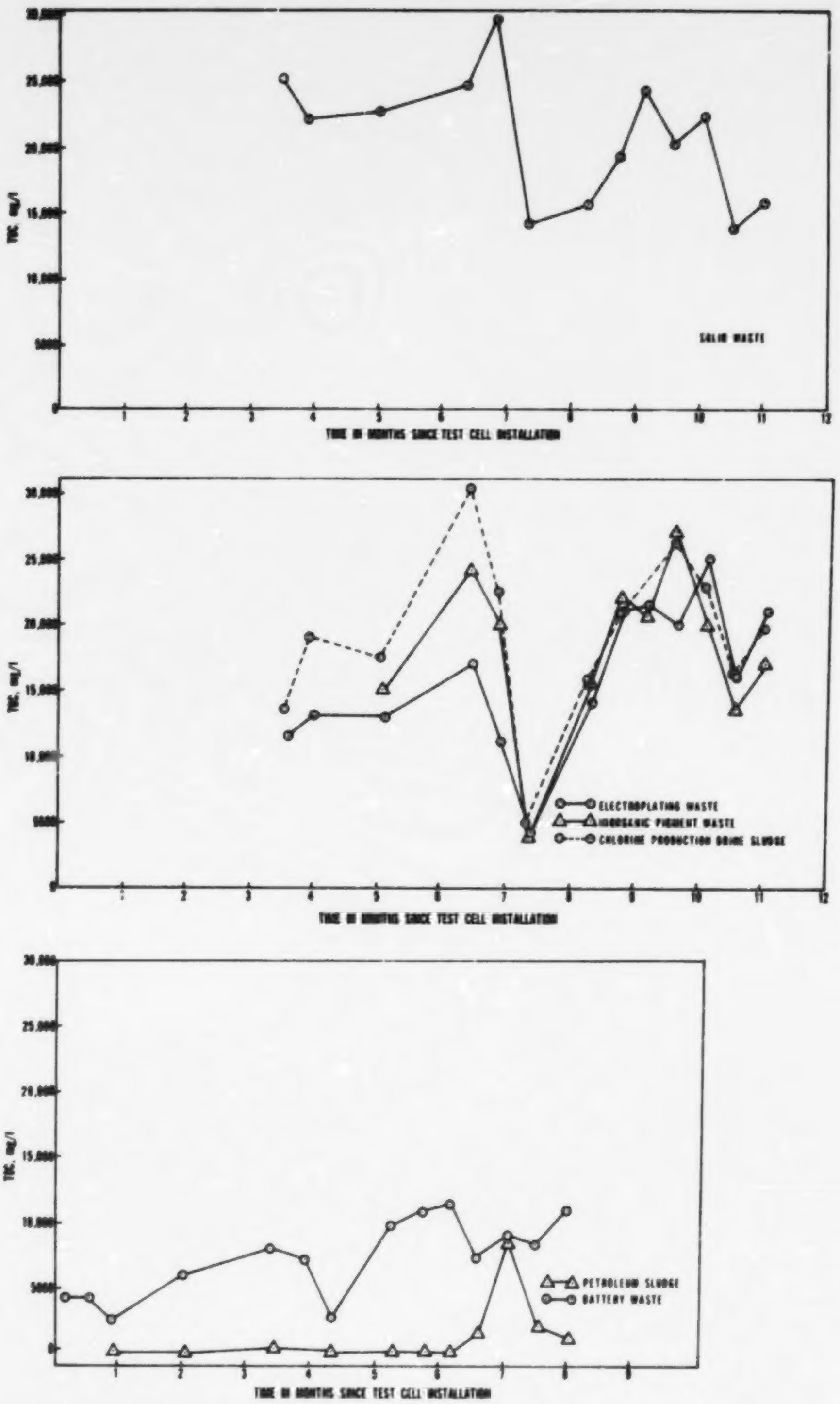

FIGURE 3. TOTAL ORGANIC CARBON CONCENTRATION IN LEACHATE

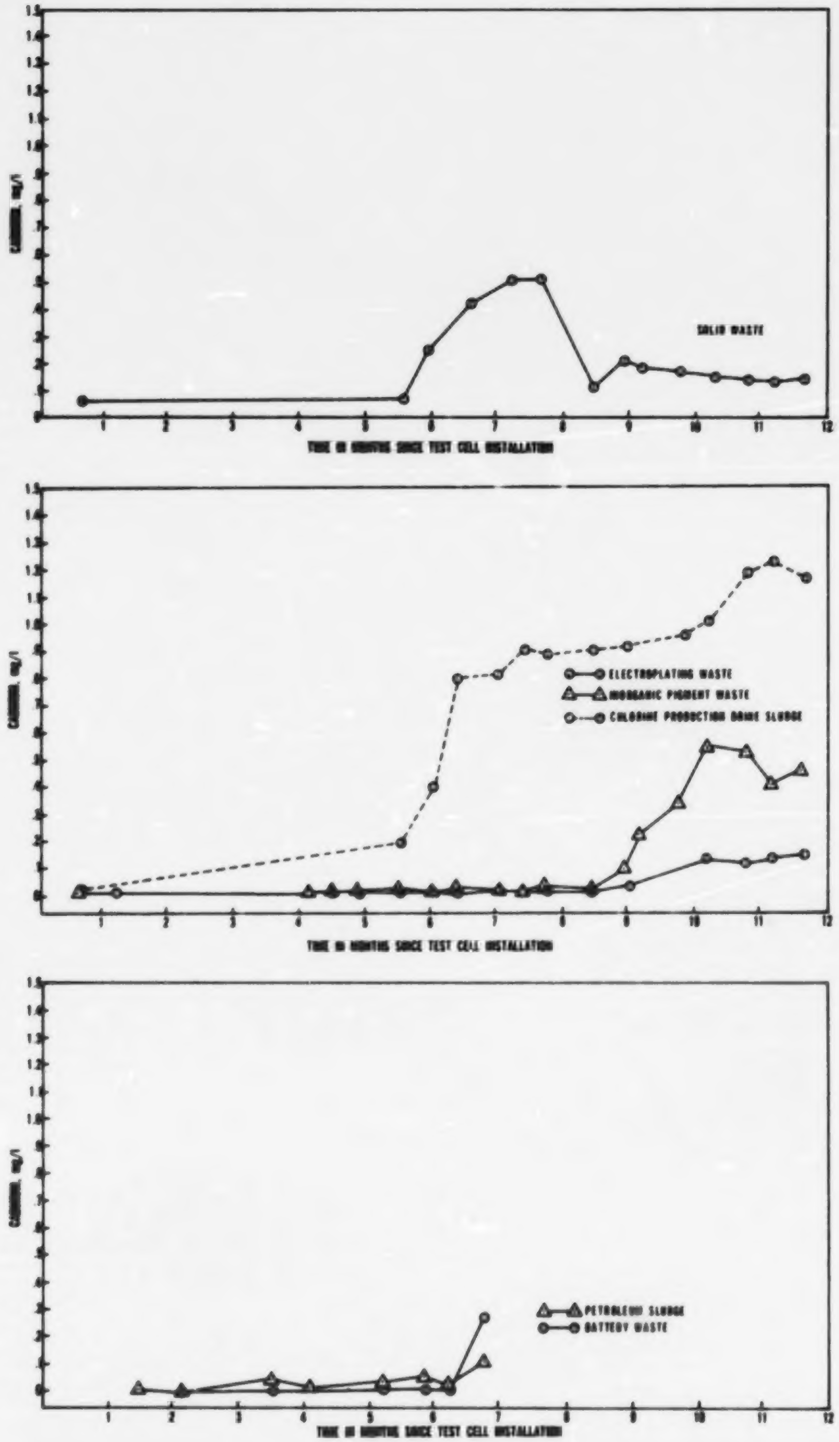

FIGURE 4. CADMIUM CONCENTRATION IN LEACHATE

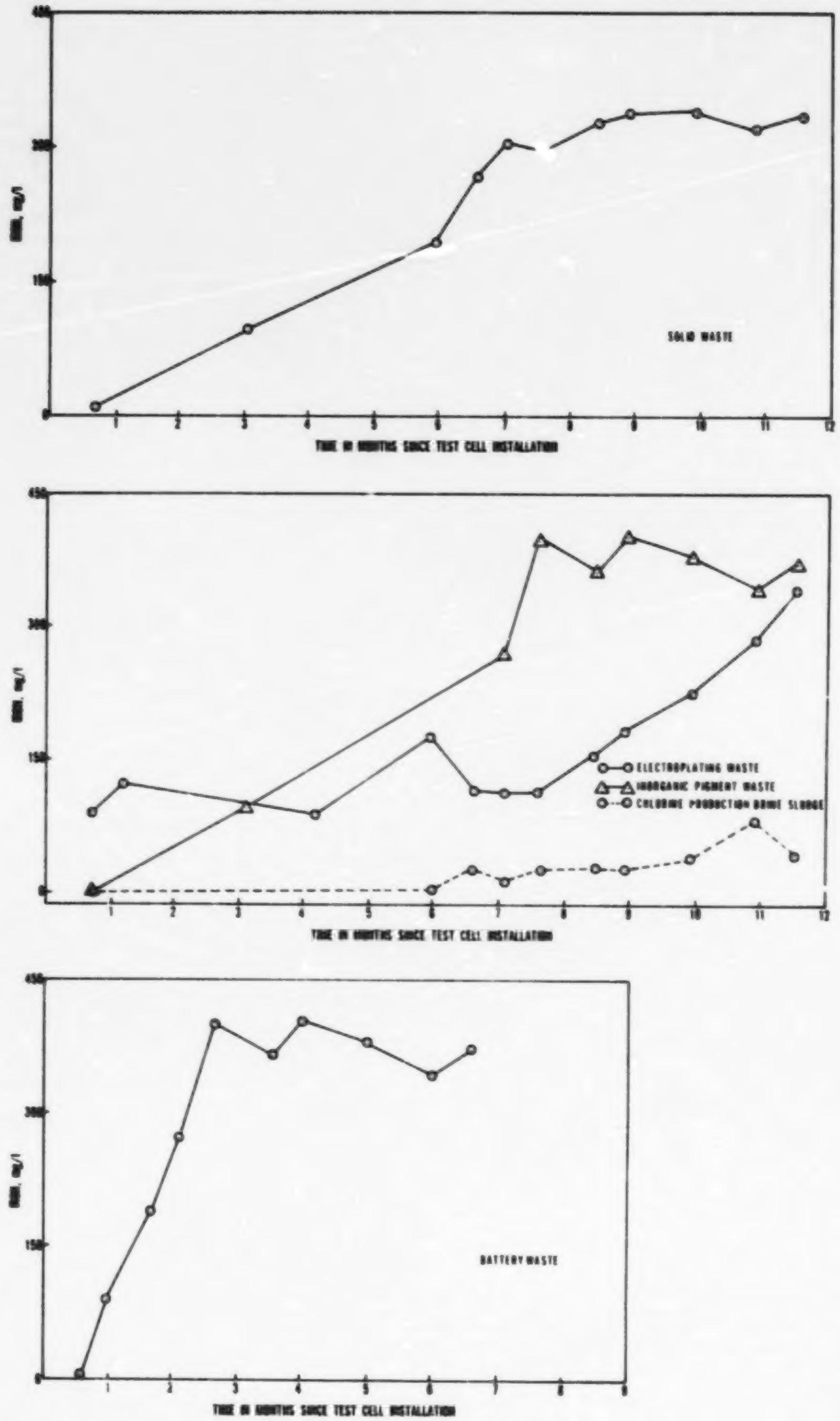

FIGURE 5. IRON CONCENTRATION IN LEACHATE

high Cl content, 10 percent, in the IPW did not impair leachability of iron from that waste stream. Inhibition of biological anaerobic activity was discounted since organic acid production was high, despite rather high contents of Pb (697 ppm) and Hg (227 ppm) in the raw sludge.

The chromium concentration histories, Figure 6, did not resemble those of the organic acids and Cd. Initial high peaks in electroplating waste and chlorine production brine sludge of 36 and 25 mg/l respectively resulted from sludge squeezings. Subsequent analyses showed a steady decline to lower levels, generally less than the 3 mg/l reported for the other refuse/industrial sludges and refuse only leachates. The latter peaked at .14 mg/l near the 9th month after placement of the waste.

The non-conformance of the Cr data to increased solubility is probably due to the absence of readily available Cr in all of the waste streams examined. The high levels leached from the squeezing of the EW and CPBS represent the removal of readily available Cr. Alternatively, the Cr may have reacted with the other waste materials and remained in the waste mass. Long term monitoring and ultimate analysis of the leached refuse on termination of the study should determine the accuracy of the latter.

Other characteristics of the leachate also were monitored, but on a less frequent basis; consequently, since leaching has just begun, sufficient data for graphical presentation is not available. Sustained maximum concentrations of several characteristics were determined, Table 3; but only those concentrations which occurred on a somewhat continual basis have been tabulated. All five of the leaching refuse/industrial sludges yielded more maxima that exceeded those from refuse than did not. Leachate from the refuse/RS showed As, B, Ni and Zn occurring at lower concentrations than found in the refuse alone. On the other extreme, the leachate from the refuse/CPBS had showed 12 contaminants exceeding those in the refuse only leachate and 10 of these were maxima for all leachates studied.

High concentrations of vanadium were found in leachates from refuse/BPW; catalysts used in the manufacture of various batteries was suspected as the source. Vanadium was also found in leachate from refuse/IPW. Its source was believed to be the ore used during processing. Generally, any sludge derived from a processing operation employing ore, rock, or salt will contain high levels of inorganic contaminants. Assays of these sludges indicated they were high in aluminum, iron, sodium, magnesium, chromium, vanadium, tin, nickel, and antimony.

Maximum selenium concentrations were found in the refuse/EW leachates even though the raw EW residuals contained the least. Antimony was detected only in the inorganic pigment waste. Tin was found in all leachates, occurring at 5 to 53 times greater in the refuse/industrial waste leachates than in the refuse leachates. Stabilizers in plastic materials may have contributed to the tin in the raw refuse.

Asbestos was found in leachates from the refuse/IPW and the refuse/CPBS. In both cases, the asbestos was found to originate from contaminants introduced to the material flow during processing operations. Surprisingly no asbestos was found in the leachate from the refuse/BPW.

Cyanide was found in the refuse/BPW leachate but was not detected in the refuse/EW despite the fact that the raw EW contained 100 times more cyanide than the BPW.

Phenols were determined by a gas chromatographic procedure which identified all phenolic compounds regardless of their substituent groupings. Approximately 4 mg/l were found in leachates from the refuse whereas 23 mg/l, or almost

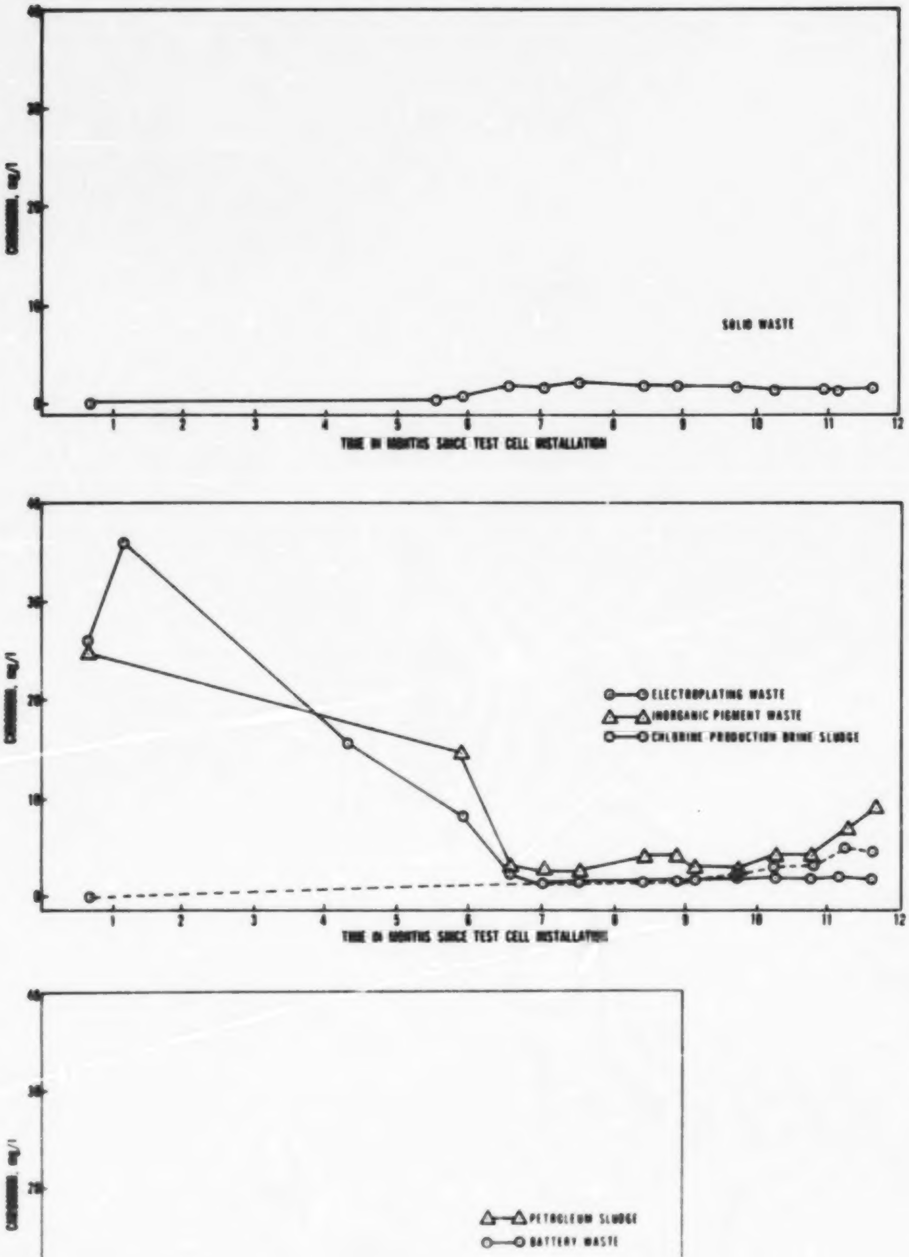

FIGURE 6. CHROMIUM CONCENTRATION IN LEACHATE

TABLE 3. SUSTAINED MAXIMUM CONCENTRATIONS OF LEACHATE CONTAMINATS[a]

Waste Cell	SW[b] 4	RS[c] 9	BPW[d] 10	EW[e] 12	IPW[f] 13	CPBS[g] 14
Vanadium[h]	<0.03	<0.03	([0.29])[i,j]	<0.03	([0.23])	<0.03
Arsenic[k]	12.2	<3.0 [ℓ]	([30.0])	<3.0	13.0	([54.0])
Selenium[k]	<5	(13)	<5	([230])	([10.0])	<5
Antimony[k]	<5	<5	<5	<5	([17])	<5
Tin[k]	150	(800)	(1200)	(3000)	(2400)	([8000])
Sulfur[h]	674	NSA[m]	491	68	(846)	([3362])
Asbestos[n]	<100	<100	<100	<100	([6000])	([3000])
Cyanide[k]	<1	<1	([1.2])	<1	5.0	<1
Aluminum[h]	<0.05	(1.2)	(8.1)	<0.05	(5.4)	([11.2])
Phenol[h]	4.3	([22.9])	NA[p]	NA	NA	NA
Beryllium[k]	<0.1	(0.9)	([45.0])	([30.0])	4.5	([48.0])
Lead[k]	1510	1450	([3380])	(1820)	(2140)	([6460])
Titanium[h]	<0.1	<0.1	<0.1	<0.1	<0.1	(0.6)
Mercury[k]	19.7	(31.2)	7.2	(26.9)	(67.1)	([328])
Boron[h]	18.1	2.8	13.3	(22.0)	(24.0)	([83.0])
Nickel[k]	1360	1010	1319	([3505])	(1490)	([6020])
Zinc[h]	4.3	2.1	(5.2)	0.5	([11.2])	(8.0)
Summation		4 (6) [1]	3 (8) [5]	3 (7) [3]	0 (13) [5]	0 ([illegible]) [10]

[a] Higher concentrations may have been detected.

[b] Solid Waste.

[c] Refinery Sludge.

[d] Battery Production Waste.

[e] Electroplating Waste.

[f] Inorganic Pigment Waste.

[g] Chlorine Production Brine Sludge.

[h] mg/ℓ

[i] ( ) indicates exceeded solid waste.

[j] [ ] indicates exceeded maximums.

[k] μg/ℓ

[ℓ] Underscore indicates less than solid waste.

[m] Insufficient sample available.

[n] Fibers/ℓ

[p] Not analyzed.

6 times that amount, were found in the refinery waste.

Beryllium was found in leachates from all the refuse/industrial sludges but was not detected in leachates from the refuse only. Highest concentrations were reported for CPBS, BPW, and EW; whereas the largest amount, detected in the raw sludges was in the IPW.

Lead was found in all leachates at generally the same level, even though the raw BPW contained roughly 100 times the lead of the other wastes.

Titanium was found only in the raw sludge of the CPBS and the leachate from the refuse/CPBS.

Mercury was found in all sludges and refuse/industrial sludge leachates, though the maximum Hg in refuse leachate was greater than in refuse/BPW leachate. Not surprisingly the greatest amount of Hg detected was in the CPBS and leachates from the refuse/CPBS.

The greatest boron quantities were also recovered in the refuse/CPBS but the raw CPBS initially contained the least.

Zinc, nickel, aluminum and sulfate were also detected in most industrial sludges and leachates derived therefrom.

It can be seen from the solid waste chemical composition, Table 4, that municipal solid waste itself contains many of the same constituents that are of concern in industrial sludges. For example the metals (Cd, Cr), glass (As), fines (Cr), ash, rock and dirt (Cr,). Other studies have indicated the presence of the following; glass (Cr, Al, B, Sn, Ti, Zn, Be and Ni), metals (Be), ash, rock and dirt (Cr, Al, B, Pb). These actions are generally present in the solid waste in the fractions which constitute the lowest percentage (i.e, metals constitute only about 10% of the total solid waste).

Gas Analyses

The gas composition of most of the industrial waste cells was relatively constant, Table 5. They recently went from the anaerobic non-methanogenic stage, (during which carbon dioxide production exceeded 90% by volume), to the early phases of methane production. One would expect to see the formation of hydrogen with a decrease in CO_2 and beginning of methane production at this time. The slow production of methane is attributed to the reduced cell temperatures which has slowed down the microbial degradation. This was verified by the higher methane production within cell 17 which was maintained in a heated bay area.

The refinery waste, as it was placed, contained large numbers of bacteria (2.4×10^4 aerobic colonies/gram). These bacteria, obviously acclimated to this waste, have begun to degrade this material at a tremendous rate as evidenced by the high methane content.

Microbial Analyses

The microbial populations within the cells changed considerably since initiation of the study. It was found that dieoff of the fecal coliform group occurred while the fecal streptococci continued to survive. More recently, fecal streptotococci showed an apparently declining trend as the industrial waste cell leachates continued to show higher metal concentrations. Additional assays will be required before any conclusive results are known.

Summary

Six selected industrial wastes admixed with municipal solid waste were placed in test lysimeters. Their effects upon leachate generation and composition, gas composition and microgiological activity was determined.

TABLE 4. SOLID WASTE CHEMICAL COMPOSITION[a]

Component	Paper	Garden	Metal	Glass	Food	PRLT[b]	Fines[c]	ARD[d]	Diapers	Wood	Composite
COD[e]	0.804	0.815	0.492	0.011	0.754	2.14	0.935	0.040	0.720	0.503	0.520
TKN	0.028	0.171	0.022	0.140	3.09	1.25	0.131	0.119	0.138	0.228	0.247
Total Phosphate	0.048	3.14	2.79	0.049	10.4	1.40	1.97	4.48	2.65	0.103	2.32
Lipids	2.47	3.04	0.420	1.54	13.8	5.02	4.85	1.52	2.26	1.00	2.84
Ash	92.0	36.5	4.85	2.25	41.6	182	49.5	19.6	96.0	77.9	25.8
Crude Fiber	21.7	16.6	0.235	0.040	10.5	21.5	6.39	5.85	13.7	20.8	11.3
Total Carbon	58.0	14.4	4.80	0.750	19.5	15.8	16.4	13.4	44.5	51.0	24.8
Inorganic Carbon	4.30	4.66	3.40	0.220	2.58	5.75	4.30	7.80	0.740	0.380	3.08
Organic Carbon	53.7	9.74	1.40	0.530	17.0	10.1	12.1	5.60	43.8	50.7	21.8
Sugar as Sucrose	<0.1	1.71	<0.1	<0.1	6.08	<0.1	1.18	<0.1	<0.1	<0.1	3.50
Starch	3.40	7.42	<0.1	<0.1	8.57	3.42	7.20	6.40	<0.1	0.78	16.2
Asbestos	NA[f]	NA	NA	NA	NA	NA	NA	NA	NA	NA	<1[g]
Arsenic[h]	<0.1	NA	<0.1	10.2	NA	NA	1.2	3.6	<0.1	<0.1	80
Selenium[h]	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	<0.1
Mercury[h]	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	5.0
Lead[h]	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	15.0
Beryllium[h]	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	<0.1
Cadmium[h]	0.36	NA	20.9	2.7	NA	1.8[i]	4.2	4.5	0.25	1.6	2.4
Iron[h]	375	330	6.25[a]	3220	505	444	0.392[a]	0.340	99.0	0.378	0.782[a]
Zinc[h]	50.0	106	175	9.75	59.0	118	322	181	343	59.4	127
Chromium[h]	8.2	1.1	15.3	1.1	1.3	2.0	13.1	10.1	0.5	1.1	10.7
Manganese[h]	13.1	194	870	15.7	12.2	12.1	115	177	5.90	50.0	90.5
Potassium[h]	11.2	0.135[a]	1.00	2.70	0.162[a]	98.7	135	555	750	90.0	475
Magnesium[h]	160	4175	80.5	472	377	289	1.02[a]	2.63[a]	279	253	0.225[a]
Calcium[h]	77.5	0.830[a]	<0.25	16.2	0.465[a]	912	2.11[a]	4.08[a]	360	590	0.437[a]
Sodium[h]	9.70	185	37.0	60.0	804	143	400	0.209[a]	0.110[a]	572	950

TABLE 4 (cont'd)

Component	Paper	Garden	Metal	Glass	Food	PRLT[b]	Fines[c]	ARD[d]	Diapers	Wood	Composite
Copper[h]	4.5	9.34	0.221[a]	2.54	8.58	12.4	35.8	32.6	4.14	38.2	31.6
Nickel[h]	15.7	15.7	115	19.0	12.5	32.0	33.2	10.1	3.36	27.0	10.1
Moisture	56.7	156.4	8.80	2.00	216.5	57.04	123	30.79	133	21.43	
Moisture[j]	35.20	56.91	6.18	1.65	70.07	49.27	49.36	18.52	66.28	17.10	
Composition	42.6	10.7	12.2	12.2	3.6	8.7	2.9	3.2	1.3	2.6	
Composition[j]	41.62	15.77	8.21	7.83	7.56	10.91	3.58	3.36	2.47	1.99	

[a] Percent by dry weight unless otherwise sepcified.

[b] Plastics, rubber, leather, and textiles.

[c] <25.4 mm (1.0 in.).

[d] Ash, rocks, and dirt.

[e] g COD/g sample.

[f] Not analyzed.

[g] Fibers per gram.

[h] Parts per million by weight.

[i] Plastics, rubber, and leather not analyzed.

[j] Percent wet weight.

TABLE 5. GAS COMPOSITION DATA[a]

Cell	Contents	O_2	N_2	CH_4	CO_2	H_2
4	Solid Waste	0.3	29.9	0.0	69.2	0.0
9	Refinery Sludge	0.2	26.4	17.1	56.1	0.0
10	Battery Production Waste	1.1	22.3	0.0	76.5	0.0
12	Electroplating Waste	0.3	16.4	1.1	81.9	0.0
13	Inorganic Pigment Waste	0.2	2.9	0.0	96.9	0.0
14	Chlorine Production Brine Sludge	0.1	16.6	0.0	83.3	0.0
17	Solvent Based Paint Sludge	0.4	47.0	4.9	41.0	6.4

[a] Percent by Volume.

A reduction in moisture adsorption capacity resulted from the addition of semi-solid industrial wastes. High concentrations of contaminants leaching from the various waste streams have been noted.

Metallic ions may respond in several ways in a landfill environment. They may:

1. Become very soluble due to the acid/reducing conditions (Fe);

2. Be initially discharged in the leachate due to already solubilized cations, or readily leached during initial placement (Cu, Cr);

3. Be converted, either chemically or microbially, to a form which is more amenable to transport (Hg).

The solid waste/refinery sludge mixture is undergoing rapid decomposition which has reduced the quantity of organic matter in the leachate. This indicates that more complete decomposition may result from the addition of certain refinery wastes to municipal solid waste.

PRACTICAL RECOMMENDATIONS FOR OIL SPILL DEBRIS DISPOSAL: A PROGRESS REPORT

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ABSTRACT

Many oil spill cleanup efforts include the disposal of a significant quantity of oily organic and inorganic debris. Because spills are emotion-charged events, debris disposal is often impeded by the somewhat exaggerated fears of local inhabitants and officials. In some cases on record, final disposal plans could not be implemented until more than a year after the spill. It is felt that a written description of the technical options might help alleviate the difficulties. The U.S. Environmental Protection Agency has retained SCS Engineers, Inc. to prepare a detailed, practical how-to-do-it manual for oil spill debris disposal and to make an accompanying film for State and local officials. A literature search has been carried out, sites for confirming field studies chosen, and some film footage taken. The bulk of the field work is scheduled for early spring. The completed manual and film are due in early summer 1976. Present recommendations for disposal of unrecyclable material include soil cultivation, incorporation into an approved sanitary landfill and individual burial. A description of the rationale proposed for selecting one method over another and findings to date are presented.

THE PROBLEM

You all have read media accounts of oil spills, seen pictures of sticky workers cleaning up blackened beaches and felt sorry for the wild birds being de-oiled by toiling volunteers. Despite the significant reduction in the number of spills, achieved in part by the effective spill prevention regulations being administered by the U.S. Environmental Protection Agency (EPA), the unfortunate truth is that oil will continue to be spilled so long as humans and equipment are involved. Published Coast Guard figures show that 11,435 spills totaling 15,808,436 gallons of oil were reported in 1974.(1)

In the course of cleaning up a spill, some oily debris is almost inevitable. The debris may be chiefly biodegradable material, such as seaweed, leaves, driftwood or grasses; or may be chiefly non-biodegradable, such as sand, gravel, shingle, rocks, beer cans, truck tires or plastic; or may be almost any combination. If a spill generates a large volume of debris, the debris may be stockpiled at one or more temporary locations until a decision about final disposal can be made.

The selection of a means of disposal should not be made lightly. First, the volume of material from a single spill may amount to as much as 10,000 dump truck loads. Next, even a small quantity of oil working its way into the drinking water supply could produce taste and odor problems. Finally, and perhaps most significant here, by this stage in a spill the local population has been semi-traumatized by the media coverage and by the shock of seeing their very own land oiled up. A typical reaction to this nightmare-come-true is to want all evidence of it far away, out of sight, instantly. The thought of having the debris remain nearby, even in the local landfill, is unthinkable. And naturally, all the other, unaffected towns in the region who've been watching the news definitely don't want the debris transported to their landfills either.

Since the debris is often stockpiled in the local swimming beach parking lot, a real sense of the urgency of the problem doesn't develop until the bathing season approaches. In some cases, the impasse remains until finally some state or Federal land can be found to receive the debris.

THE PROPOSED SOLUTION

Several EPA regional spill cleanup coordinators have expressed the feeling that state and local officials would be greatly assisted in their efforts to dispose of the oily debris locally if a written, rational, practical, state-of-the-art description of the options were available. Such a document, especially if Federally sponsored, would provide a comprehensive source of authority which local officials could rely upon for support in making their technical and political decisions.

In late June 1975 the EPA Oil & Hazardous Materials Spills Branch in Edison, New Jersey retained SCS Engineers to prepare a practical, state-of-the-art, how-to-do-it manual for the land disposal of oily debris. The manual is to be based both upon an extensive literature search and upon confirming field work. The manual is to contain:

a. A thorough discussion of the scientific and engineering rationale (cross-referenced to published literature and site visits performed under this contract) for selecting these recommended detailed directions.

b. Detailed directions for selecting sites at which oil spill cleanup debris may be disposed of in an environmentally safe manner.

c. Detailed directions for preparing the sites and for placing and treating oil spill cleanup debris at the sites selected in an environmentally safe manner.

d. Detailed directions for operating the site and reworking the oil spill cleanup debris deposited there (if desirable and/or necessary) so as to ensure minimal environmental damage and maximal environmental benefits.

e. Detailed directions for monitoring the oil spill cleanup debris, the disposal site and its vicinity so as to be able to detect any possible environmentally damaging situation early.

f. Detailed directions for remedial measures to correct those potentially damaging situations discovered by the monitoring.

g. A thorough discussion of the potential benefits and damages that may result from adhering to the above directions.

h. An appendix containing the outline of a suggested training course for disposal site operations personnel in these techniques recommended for disposing of oil spill debris.

i. A technical appendix containing a detailed account of sites visited, information gathered, field work performed, data obtained and conclusions drawn, together with the rationale for the actions undertaken.

In addition, SCS is to prepare a short, color summary film for State and local officials. Both the film and the manual are scheduled for completion in early summer 1976.

PROGRESS TO DATE

Literature Search

The chief objective of the information gathering phase is to determine the state-of-the-art of knowledge of the environmental effects of oil spill debris disposed of on land. Efforts were organized to obtain the following information:

- Properties of oil spill cleanup debris;
- Integration of oil and oil emulsions with soil;
- Degradability of oil spill cleanup debris;
- Effects of oil disposal on vegetation; and
- Status of existing oily waste disposal technology.

Materials from the literature were, and continue to be, expanded and supplemented by data gathered through personal interviews with various knowledgeable representatives of industry, government, and the academic community. A number of spills and spill sites, debris disposal areas, refinery waste disposal areas and disposal method test plots have also been visited.

Field Studies

Because most of the literature-based information and data obtained from personal interviews were not specific to oil spill debris, field studies are planned to try to obtain information pertinent to oil spill debris disposal sites and to confirm ideas in the literature.

Three case study sites have been selected. The first site is in northern California and involves straight burial. The second is in Rhode Island and involves an above-ground landfill. Both of these contain oil spill debris only. The third site is in Utah near the Great Salt Lake, involves the soil cultivation of lube oil from a waste lagoon and will be described by Hal Snyder and George Rice in an interesting presentation tomorrow.

We would like to find a fourth site to investigate, but are having difficulty in locating interesting ones about which sufficient background information exists. If any member of the audience has a suggestion, please contact us.

The field work will begin this March. Soil and debris samples will be collected both from the surface and during the drilling of about 5 wells at each disposal site. Soil and oil spill debris samples will be analyzed for oil content, total extractable hydrocarbons, various ions, and biological activity. Soil samples will also be tested for permeability and grain size distribution. In addition, water and leachate samples will be collected where appropriate and analyzed primarily for oil content.

The samples will help determine:

a) whether the oil remains at the disposal site
b) how much oil is present
c) the character of the oil at different locations within the site.

From these, an assessment of the effectiveness of the disposal method may be made.

Film Making

Some background film footage has been obtained. The main work will be accomplished this spring.

PRELIMINARY CONCLUSIONS

On the basis of information reviewed and interviews conducted thus far during the project, the following conclusions can be drawn.

1. Knowledge of important aspects of oily waste interaction with the environment is generally lacking. Various tests have been run at refineries and elsewhere indicating that natural vegetation reestablishes itself on oily waste treated plots within one growing season. Relatively little work has been done regarding the effect of oily wastes on vegetation growing on a disposal area. Some reports indicate that food crops may be grown and safely eaten as little as three years after oil has been placed on the soil. Others suggest that no edible crops should ever be grown on oil-treated lands. This question requires resolution.

2. Only limited study of oil spill debris disposal or of the debris' effects on the environment has been conducted to date. However, existing information on

land disposal of oily refinery wastes and crude oil is applicable to the problem of oil spill debris disposal.

3. Debris from a single oil spill may consist of either essentially one material or a large variety. The range of sizes of components may be widely varied or the reverse. The debris itself may or may not be largely biodegradable.

4. The oil mixed with the spill debris may have a relatively high metals content if it has been used for lubrication, and its other properties may vary over a wide range depending upon its origin and history. The quantity of oil mixed with the debris may range from almost none to over 10 percent.

5. An attempt should be made to find a use for as much of the debris as possible. Examples of uses are oil reclamation and road bed construction.

6. Oil is an organic substance and as such is subject to biodegradation. Biodegradation occurs fairly readily under aerobic conditions. Oil degradation in an anaerobic environment is at best very slow, and "buried oily waste will remain unchanged for hundreds of years."(2) Over 100 species of bacteria and fungi commonly found in the Temperate Zone are known to attack one or more fractions of crude oil. Suitable oxygen, nutrients, water, and temperatures are also required. Data regarding oily waste degradation rates have been obtained primarily from studies of relatively homogeneous refinery waste. Oil spill cleanup debris may be very different from oil refinery waste and may or may not exhibit the same degradation rate characteristics. Studies have shown that oily wastes continually exposed to oxygen have degraded to relatively imperceptible levels of oil in periods ranging from a reported six months up to three years. The actual time depends upon disposal methods, oil type, climate, and other site-specific factors. Degradation rates on the order of 800-1000 barrels pure oil per acre per year have been achieved.(2)

7. The soil cultivation process has been used routinely for years to dispose of oil refinery tank bottoms and separator sludge wastes. Initially, the land is cleared, fertilizer added and the area roto-tilled to break up clumps and distribute the fertilizer. A 6 inch thick layer of sludge is added (dumped from trucks at the edge of the field and distributed by bulldozer) and left to de-water by evaporation. When de-watering is largely complete (several weeks), the sludge is roto-tilled to mix it thoroughly and evenly into the soil and fertilizer. Roto-tilling is repeated at varying intervals (from bi-weekly to quarterly) during the growing season. The initial amount of fertilizer and any later additions depend upon the results of soil analyses. Roto-tilling provides better mixing and is definitely superior to disking. The size and nature of the debris must be such that it will not damage the roto-tiller. Oil degradation will be slower during the first season until the bacteria numbers build up. Degradation is often essentially complete in less than three years. Because of various uncertanties, it seems best at the present time to recommend that no edibile crops be grown on land used for soil cultivation of oil. Considerable land exists which has a low slope and is not suitable for pasturage or crop production. In more built up areas, soil cultivation can be practiced on top of completed portions of landfills if suitable precautions are taken to prevent penetration of the upper impermeable layer. Some 8,000 cubic yards per year of refinery separator sludge have been handled in a 16 acre coastal Texas site.(3)

8. Oil spill debris may be incorporated into existing sanitary landfills or a specially constructed landfill, or buried. In these anaerobic environments the oil will degrade only slowly at best. Because the potential for leaching is present for decades, it is felt that these disposal methods are inferior to the soil cultivation process. Measures must be taken to ensure that leachate can never migrate from the site. Careful site design and proper materials of construction can reduce the problem. These disposal methods do have the advantage that they can accept both large individual pieces of debris and non-biodegradable synthetic materials. If one of these anaerobic disposal methods is to be used, an existing sanitary landfill (assuming it is properly sited, constructed and operated) is the first choice because the land has already been committed to disposal operations. The other two methods require the diversion of "new" land.

9. Research into the interaction of oil and the environment is increasing rapidly. Spurred by the public's concern over oil spills and environmental pollution in general, refineries and universities are investigating more intensely the pertinent factors. This suggests that systems presently recommended for land disposal should be reviewed periodically in the light of new data that may be developed.

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INDUSTRIAL HAZARDOUS WASTE MIGRATION POTENTIAL

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ABSTRACT

The migration of hazardous materials in soil is largely controlled by the physical and chemical composition of the soil upon which the waste is placed. However, differences in waste composition and leachability cause large differences in migration of specific elements or compounds through a soil. This is demonstrated by comparing the migration of cadmium, leached from four different industrial wastes, through one type of soil. The wastes were nickel-cadmium battery, electroplating, water base paint and inorganic pigment wastes. The soil used in these experiments was Davidson (N. Carolina) clay soil which is classified as an Ultisol. Information as to difference in penetration and distribution of the cadmium in the soil is presented and related to differences in the wastes.

INTRODUCTION

Industrial processes along with air and water pollution abatement activities generate tremendous and ever increasing amounts of solid and semi-solid wastes which are disposed of in lagoons and landfills. These wastes often contain hazardous substances that can be released from these wastes by leaching or decomposition, and then migrate down through the soil into potable water supplies. Instances have been reported of human and animal poisoning due to leaching of toxic substances from wastes placed in disposal sites and subsequently migrating into underground water (1,2,3). It is therefore important to examine the potential of these toxic materials to move through various types of soil.

The migration of toxic substances is influenced by the chemical and physical composition of the underlying soil. However, the chemical composition of the waste itself establishes the ionic exchange capabilities of the resulting leachate, which can produce vast differences in the migration of a toxic substance even through one type of soil. The effect of waste is shown here by leaching four different industrial wastes with water and following the migration of cadmium through a clay soil. (Cadmium was chosen as an example from a larger study where a number of toxic metals were leached from industrial wastes by water and by landfill leachate and passed through two types of soil.)

METHODS AND MATERIEL

Description of the Industrial Wastes

Nickel-Cadmium Battery Production Waste

This waste arises from the washing of nickel and cadmium electrodes. The washings are quite alkaline (pH 11-12) and contain nickel and cadmium hydroxide precipitates. Most of the precipitates are reclaimed. However, some "fines" are lost in the waste water. The industrial plant where the samples were collected disposes of the wastes in a lagoon. The first waste sample was collected from the lagoon at the outfall of the waste line. A second waste sample was collected from the lagoon itself. It was found that the waste "ages" rapidly in the lagoon and a considerable quantity of the excess basicity is washed out during standing in the lagoon. When a sample of aged waste was mixed with water in a ratio of one part waste to two parts water, the resultant pH was 9.1. Fresh waste mixed in the same proportions gave a pH >11. This shows the results of aging and also demonstrates differences that are likely to occur in samples from a single location. The waste sample from the lagoon was used in this study.

The cadmium content of the waste was 52 percent by weight. The cadmium was most probably present in the waste as the hydroxide salt.

Electroplating Waste

The electroplating waste results from plating, phosphatizing, and metal cleaning operations. Metals are precipitated from the waste water by the addition of lime or caustic soda. The cadmium content in the waste was 0.8 percent by weight. The cadmium probably exists in the waste as the hydroxide. However, it may also be present as cyanide complexes. A trace of cyanide was found in the waste.

Inorganic Pigment Waste

Pigment manufacture waste water containing dissolved and suspended solids is adjusted with sulfuric acid to pH 3. Sulfur dioxide is added to reduce the hexavalent chromium, the pH is raised to eight with slaked lime, sodium sulfide is added, and the excess sulfide is precipitated by ferrous sulfate. A flocculating polymer is then added, the precipitate filtered off and the liquid is discharged. The cadmium content of the filter cake is 0.17 percent by weight. The cadmium is probably present in several forms in the waste. Some may be hydroxide salts and some may exist as cadmium sulfide or other cadmium pigments.

Water Base Paint Waste

Waste and equipment washdown waters are treated with sodium sulfite, slaked lime is added to adjust to pH 10, alum and a flocculating polymer are then added and the mixture is allowed to settle. The liquid is discharged and the solids pumped into a lagoon. The cadmium content in the dried waste was very low, 0.05 percent by weight. The cadmium probably results from the pigments added to the water base paint and is in the forms previously described under pigment waste.

Preparation of Waste Columns

The wastes and the soils were packed in separate columns to allow tapping off samples of waste column leachates (Figure 1).

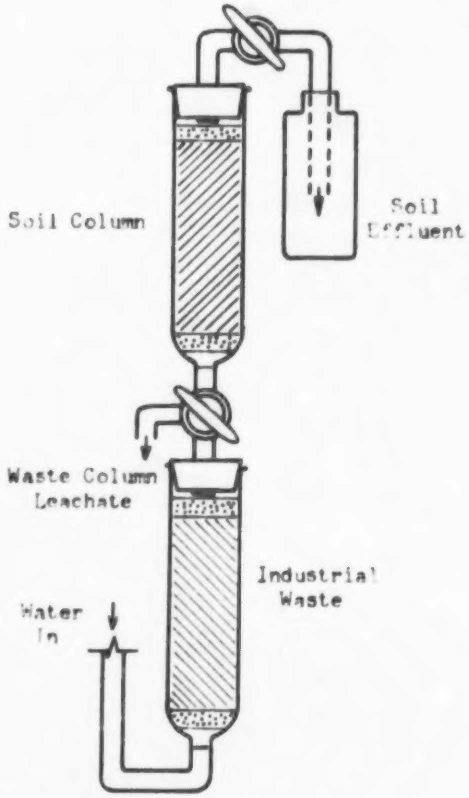

Figure 1. Column configuration.

The columns were made from 37 mm I.D. glass tubing with a 8 mm diameter tip on the bottom. A piece of glass wool was placed over the bottom hole and covered with washed quartz sand. One hundred grams of the waste were then packed into the column, occupying a depth of 10-13 cm, depending upon waste. The waste was covered with 1 cm of sand and a thin layer of glass wool and then fitted with a stopper containing a 3-way stopcock which allowed either sampling the leachate after it passed through the waste or directing it on an upflow path into the soil column above. An upflow arrangement was used to maintain saturation, to minimize channeling, and to permit better flow control at the desired flowrate of 0.5 to 1.5 pore volume per day.

The ease with which water penetrated the waste column varied greatly between the wastes. At the 7 foot head pressure used for these experiments, water quickly penetrated the water base paint and inorganic pigment wastes, but passed through the fine, densely packed electroplating waste very slowly. The nickel-cadmium battery waste was so impervious that it was mixed with an equal weight of washed quartz sand to obtain a useful flowrate.

Description of Soil

Davidson soil, an Ultisol, was used in this investigation. It is a dark red, clayey, Kaolinitic, thermic Rhodic Paleudult that was collected from the B-horizon at a depth of 30 to 100 cm by personnel from the Department of Soil Science, North Carolina State University, Raleigh, North Carolina. This soil is slightly acid and contains over 60 percent clay; the remainder is evenly divided between silt and sand. Water penetrates columns of this soil at a moderate rate.

Preparation of Soil Columns

Davidson soil was dried, mixed, and sieved to remove roots and stones, using that which passed a 20 mesh screen. Columns were packed with 160 g of soil to a density of 1.5 g/cc which gave a 10 cm depth. The pore volume calculated for this amount of soil was 38 ml, after deducting 10 percent of the volume as being unexchangeable with water percolating through it.

Analyses

Column Eluates

The pH and electrical conductivity were measured in each sample, HNO_3 was then added and the cadmium content determined by atomic absorption spectrophotometry using an air-acetylene flame. The lower detection limit for waste leachates and soil digestates was 0.02 mg Cd/l. Little interference in the analysis was found when cadmium was added to control soil leachates or soil digestates.

Soil Digestion

At the completion of each leaching experiment, the soil column was frozen and cut into four equal sections. The first section (first to receive the waste leachate) was further divided in half. Each section was dried at 105°C, weighed, pulverized, and blended. A one gram sample of each section was transferred to a 400 ml beaker, 20 ml of fresh aqua regia was added, the beaker covered with a watch glass, and the sample digested by boiling to incipient dryness. After cooling, the watch glass and beaker wall were washed down with distilled water and the volume was adjusted to 25-30 ml. Two ml of concentrated HNO_3 were added and the sample brought to a slow boil for 15 minutes. Upon cooling, the sample was filtered through Whatman 40 filter paper into a 100 ml volumetric flask. The residue was washed with 1N HNO_3 and then 5 times with distilled water. The filtrate was diluted to 100 ml and analyzed by atomic absorption spectrophotometry.

RESULTS AND DISCUSSION

Preliminary Waste and Soil Studies

There is a large difference in the solubility of various components contained in the wastes. Table 1 shows the total solids dissolved from a 1:2, waste:water slurry that was mixed for 24 hours.

TABLE 1. DISSOLVED SOLIDS

Waste	Total Dissolved Solids (mg/l extract)	Percent of Original Waste
Ni-Cd Battery	3,270	6.53
Electroplating	1,530	3.07
Pigment	540	1.08
Paint	470	0.93

The electroplating waste is about half as soluble as the battery waste while the pigment and paint wastes are far less soluble. However, significant portions of the pigment and paint wastes are organic. This may be responsible for the reduced water solubility.

The water soluble fraction of the paint and pigment wastes were analyzed for carbon and nitrogen, giving the results in Table 2. These indicate that some of the organics in the wastes are water soluble.

TABLE 2. CARBON AND NITROGEN CONTENT OF WATER EXTRACTS

Waste	Percent Carbon	Percent Nitrogen
Pigment	2.3	0.7
Paint	16.5	0

Preliminary studies were conducted using five different soils to determine which soil removed the largest amount of cadmium from the waste leachates. The soils used in addition to Davidson were Kalkaska, Anthony, Chalmers, and Nicholson. Davidson was found to be the most effective; this is somewhat surprising because its clay fraction is predominately kaolinite. The soil has a relatively low exchange capacity (9 meq/100 g). In contrast, Nicholson soil contains a large clay fraction composed predominately of vermiculite and has a high exchange capacity (37 meq/100 g). However, it has been suggested by Fuller (4) that iron present in soils is effective in removing some metals from waste leachate. Davidson soil contains 17 percent ferric oxides (5).

Soil Column Studies

Nickel-Cadmium Battery Production Waste

Figure 2 shows that a high concentration of cadmium was leached from the nickel-cadmium battery production waste throughout the study, starting at approximately 28,000 µg Cd/pore volume and gradually decreasing to approximately 8,000 µg Cd/pore volume after 26 pore volumes of water had passed through the waste column. This high challenge to the soil resulted in substantial quantities of cadmium penetrating the soil column after only two to three pore volumes.

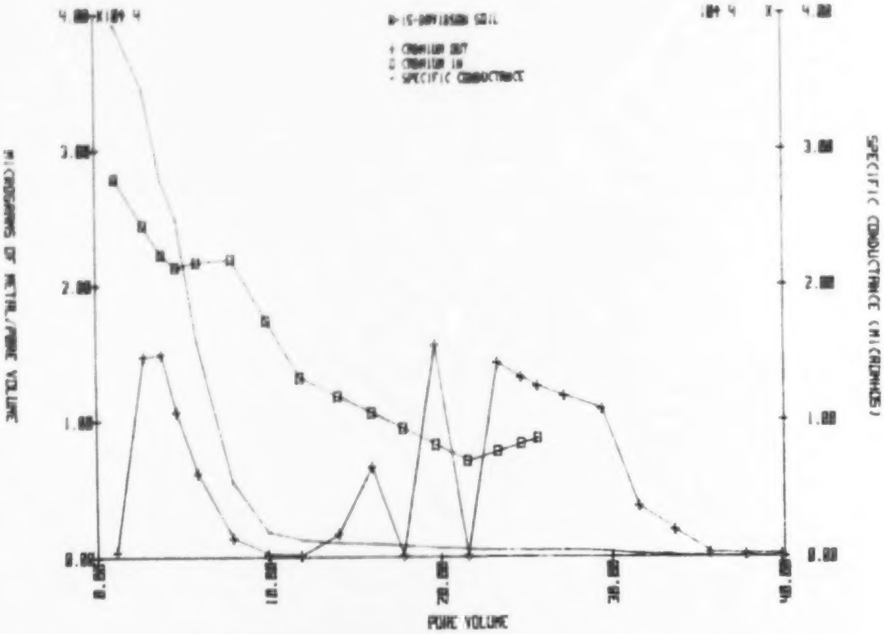

Figure 2. Penetration of Cadmium Leached from Nickel-Cadmium Battery Wastes Through Davidson Soil.

The amount penetrating increased until five pore volumes had passed through the soil and then steadily decreased to a low level for the next eight pore volumes. Apparently, the cadmium was competing initially with other soluble materials in the waste leachate for absorption and/or exchange sites resulting in a substantial quantity washing through the soil. This is indicated by the specific conductance of the soil effluent which initially was very high (40,000 micromhos) but which decreased rapidly during the next ten pore volumes. Similarly, the amount of cadmium penetrating the column dropped off even though the challenge concentration remained very high and fairly steady. Most of the cadmium was absorbed until the soil became saturated and then breakthrough was observed. If we use the definition of "breakthrough" as that point when the concentration of metal in the soil effluent equals the concentration of metal challenging the soil column, breakthrough was achieved after 19-23 pore volumes.

Shortly after it was established that the soil was saturated with respect to cadmium, the waste column was removed and the soil column was flushed with distilled water. This was done to gain information as to how cadmium flushes from a soil saturated with it. The results are shown in Figures 2 and 3.

After the water leach was started, the cadmium content in the soil effluent remained very high for four to five pore volumes. The level then dropped sharply to a relatively low level. The water flush was continued for 100 pore volumes. The cadmium concentration stayed at approximately 100 mg Cd/pore volume for 50 pore volumes, then increased to 250-300 µg Cd/pore volume and remained at this concentration until the experiment was ended. The specific conductance of the soil effluent paralleled closely the cadmium content in the flush samples.

Although the cadmium breakthrough, as defined, did not occur for 19 pore volumes, the safe drinking water level (0.01 µg/l) was exceeded continuously (6). This is also true of the cadmium found in the soil effluent collected during the water flush.

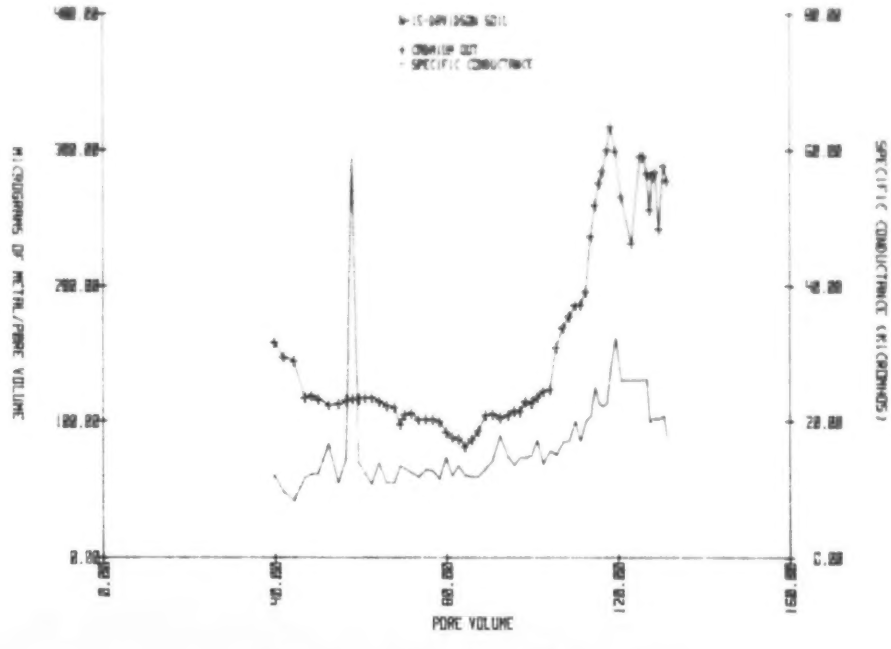

Figure 3. Water Flush of Cadmium from Davidson Soil.

This demonstrates the migration potential of cadmium from the waste and indicates the hazard that might result from improper disposal.

At the end of the experiment, the soil column was frozen, sectioned, and the soil digested. The amount of cadmium in the soil was found to be very high and fairly uniformly distributed except for the first half section. The cadmium in this section was the lowest due to the prolonged water leach. The results are shown in Figure 4; they provide some insight into the problem of reclaiming a disposal site if the underlying soil became saturated with components from a highly soluble waste.

For comparison, and to re-emphasize the importance of the soil underlying a disposal site, Figure 5 shows the ease with which cadmium breaks through Kalkaska soil, which is about 90 percent sand. The challenge concentration was similar to that used during the Davidson soil experiments. Breakthrough occurred within the first pore volume as compared to 19 pore volumes with the Davidson soil column.

Electroplating Waste

The cadmium leached from the electroplating waste behaved much differently for Davidson soil as shown in Figure 6. Although the cadmium challenge concentration was considerably lower than that from the battery waste, the soluble ion content was initially very high (conductance was 25,000 micromhos). An initial surge of cadmium leached from the waste but it reached a steady level after eight pore volumes. The soil did not become saturated with cadmium even though the waste challenge was continued for 30 pore volumes. This indicates that cadmium from the electroplating waste is fairly immobile in Davidson soil. The concentration of cadmium in the soil effluent was very low (1-5 μg/pore volume) and nearly uniform throughout the challenge period. When the column was placed on water flush, the cadmium concentration in the soil leachate samples dropped immediately to below the detection limit of the atomic absorption method.

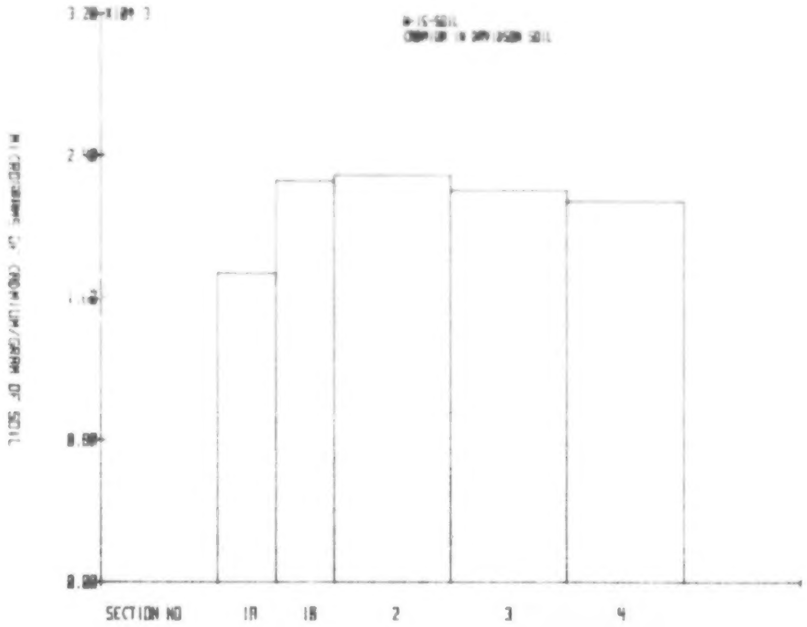

Figure 4. Distribution of Cadmium from Nickel-Cadmium Battery Waste in Davidson Soil Column.

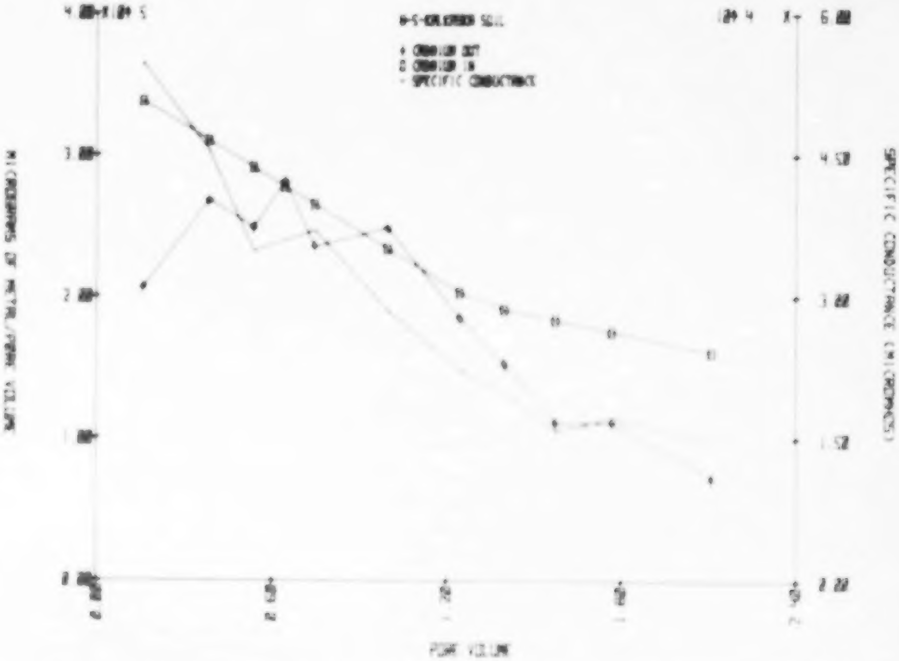

Figure 5. Penetration of Cadmium Leached from Nickel-Cadmium Battery Waste Through Kalkaska Soil.

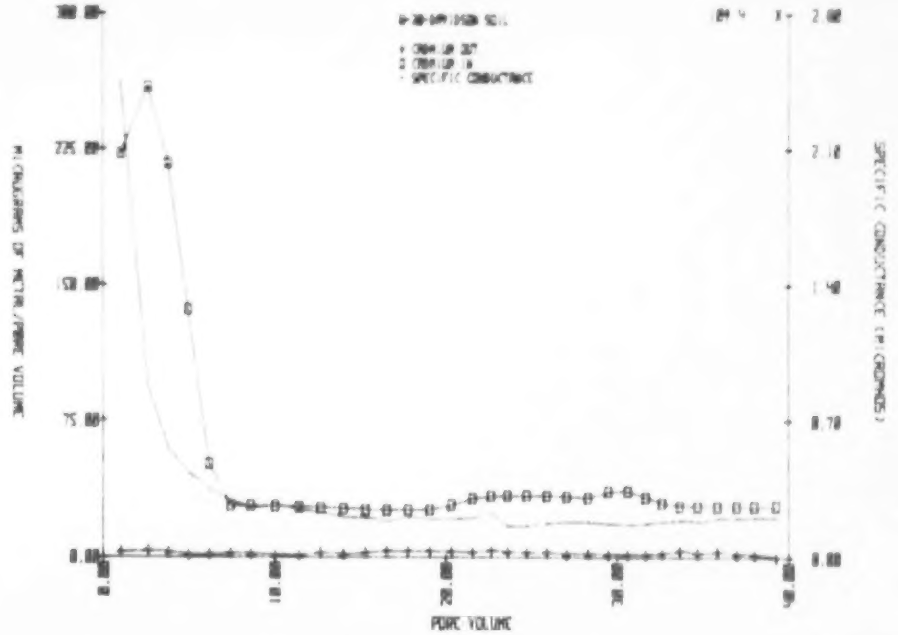

Figure 6. Penetration of Cadmium Leached from Electroplating Waste Through Davidson Soil.

As seen in Figure 7, when the soil column was sectioned and digested nearly all the cadmium was retained in the first half section, with only a small amount distributed in the second half section. The cadmium found in sections 3 and 4 was the same as that found in control columns of Davidson soil that were flushed with a comparable volume of water. This shows that the soil has the capacity to absorb a great deal more cadmium leached from this type of waste. It must be remembered that the waste initially contains many soluble ions. However, this did not result in a early burst of cadmium penetrating the soil. The cadmium is probably attenuated in the soil through absorption. However, precipitation may also account for part of the attenuation. Because of the low level of cadmium leached from the waste after the first eight pore volumes, it is concluded that little hazard would result from cadmium contained in this type of industrial waste.

Inorganic Pigment Waste

Completely different results were obtained from the studies using inorganic pigment and water base paint wastes. A much lower cadmium challenge was obtained from both wastes and the specific conductances of the soil effluents were much lower.

The results from the pigment waste study are shown in Figure 8. The initial output of cadmium in the waste leachate decreased gradually to the detection limit (1 μg Cd/pore volume) after 40 pore volumes. Cadmium came through the soil column after 15 pore volumes and its concentration in the soil effluent remained higher than the challenge concentration for the next 15 pore volumes. After a total of 40 pore volumes of waste leachate had passed through the soil, cadmium decreased to a non-detectable level except for some penetration at 83 pore volumes.

Digesting the soil after completing the challenge period revealed that no cadmium was retained on the Davidson soil.

The results obtained from challenge studies using water-base paint waste are shown in Figure 9. The cadmium content in

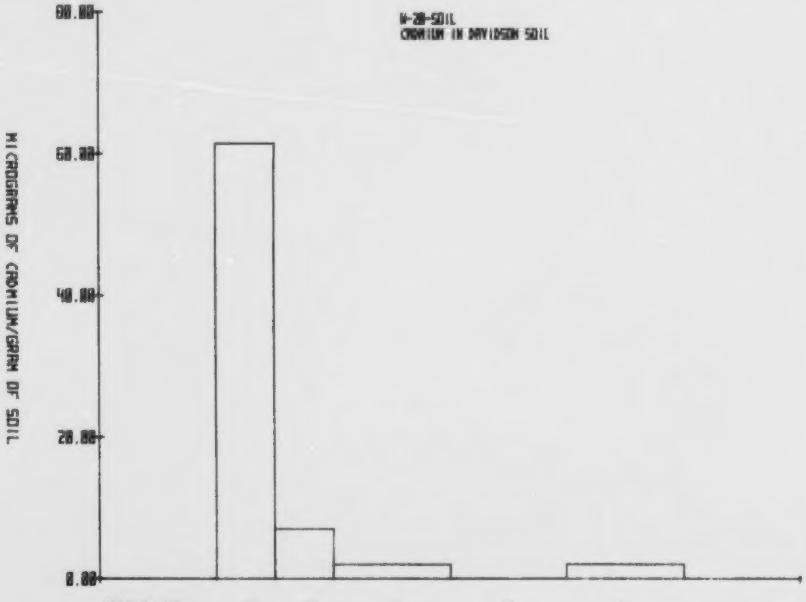

Figure 7. Distribution of Cadmium from Electroplating Waste in Davidson Soil.

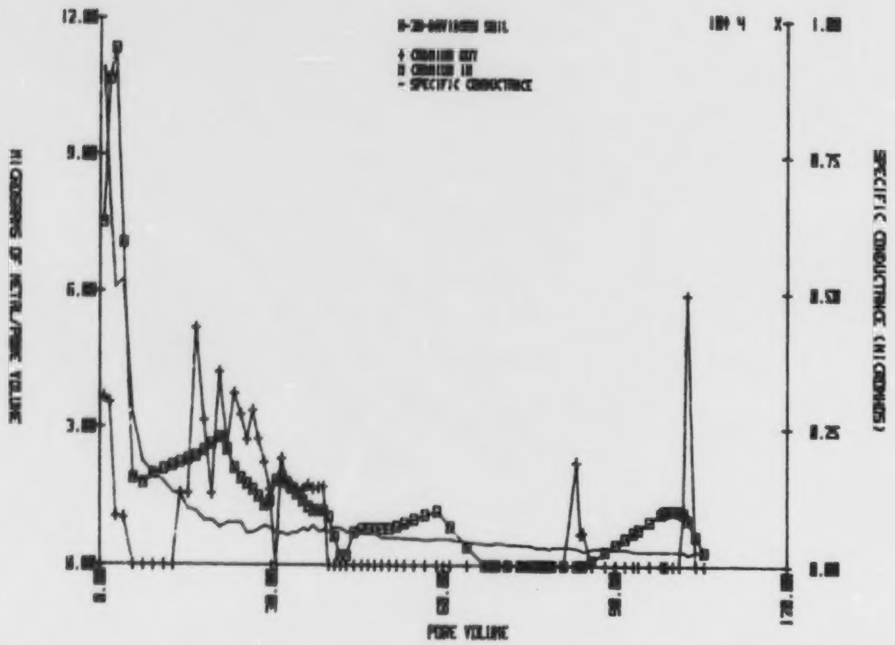

Figure 8. Penetration of Cadmium Leached from Pigment Waste Through Davidson Soil.

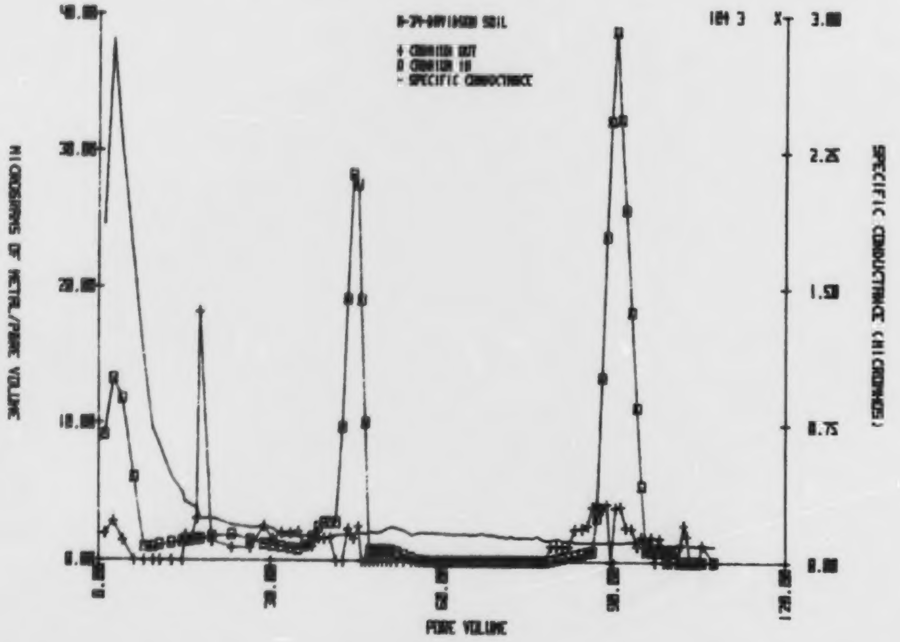

Figure 9. Penetration of Cadmium Leached from Water Base Paint Through Davidson Soil.

the waste leachate was generally low to non-detectable except for periodic surges that probably occurred as the waste composition changed through leaching. The cadmium in the soil effluent was generally low, remaining near or below the detection limit but often exceeded the challenge concentration.

These results indicate that little cadmium-ion hazard would result from the disposal of these last two wastes on Davidson soil. They also indicate that the organic fraction may play an important role in reducing the migration attenuation potential of the soil, an effect that should be examined further.

CONCLUSIONS

Various industrial wastes contain hazardous metallic ions. However, specific metals leach differently from the wastes depending upon the type of salt or complex in which the metal exists. The composition of the leachate and its solubilizing and exchange characteristics determines how a specific metal migrates through a given soil. Metals previously absorbed on the soil may also be flushed off by a change in the leachate. Components in highly soluble wastes can rapidly exceed the absorption and/or exchange capacity of the soil and cause a serious water hazard, but sparingly soluble wastes usually present less of a hazard. This work emphasizes the need to ascertain the potential of specific metals to migrate through various soils when carried by leachates having different compositions.

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(6) Environmental Protection Agency, "Interim Primary Drinking Water Standards", Mar 1975, Federal Register, Part II, Vol. 40, No. 51:11990.

FIELD SURVEY OF SOLID WASTE DISPOSAL SITES: A PRELIMINARY REPORT

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ABSTRACT

The vertical migration of chloride (Cl), total organic carbon (TOC), chromium (Cr), copper (Cu), and cadmium (Cd) in the soil below a sanitary landfill was investigated. Soil samples were taken at the municipal waste-soil interface, at groundwater, and at several intermediate depths. Soil samples were extracted with both distilled-deionized water and hot 8N HNO_3. Results indicated that the soluble species, as represented by Cl, had migrated completely through the profile. The data indicated that the refuse in the landfill was exerting a significant influence on the migration of Cr, Cu, and Cd through the soil. The formation of unknown complexes of Cd, Cr, and Cu with constituents contained in the leachate from municipal refuse resulted in their migrating deeper into the soil profile when compared to soil in the natural state.

INTRODUCTION

The ultimate recipient of many types of municipal and industrial solid waste is the land. Within the disposal site biological, chemical, and physical processes may act on these solid wastes to release contaminants from them to the air or water. Conversely, under proper conditions, chemical, biochemical, and physical processes may serve to reduce contaminant concentrations or chemically alter contaminant toxicity, reducing their potential threat to the environment. This paper is a preliminary report of potential pollution of the groundwater and vertical migration of several selected constituents at a sanitary landfill located in the upper midwest.

METHODS AND MATERIALS

Site Description

The site was given the designation number 01. Site number 01 was first opened in 1947 as an open dump and later changed to a sanitary landfill. The trench method of filling was adopted in 1950 and operated as such until the site was closed in 1960. The refuse placed into the sanitary landfill was not compacted but was covered with a 16-inch layer of soil. A total of 28 trenches were eventually filled. Trench positions at site 01 are illustrated in Figure 1.

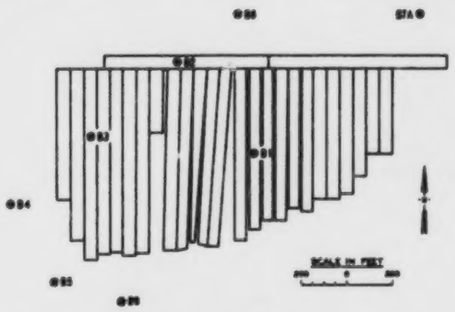

Figure 1. Municipal refuse disposal site and boring location at site 01.

Three boring/sample locations were positioned in the landfill and five outside the landfill. The three borings in the landfill were designated B1, B2, and B3. Two borings designated B6 and B7A were located on the anticipated "updip" side of the hydraulic gradient. Three borings were also located on the anticipated "downdip" side of the hydraulic gradient and were given the designations B4, B5, and B8. The borings located in the landfill were placed in trenches that were filled in 1951 (B1), 1957 (B3), and 1960 (B2). The boring locations are also illustrated in Figure 1.

Soil Sampling Procedures

Soil samples were taken at the landfill-soil interface, immediately above the water table, and at several intermediate depths. It should be noted that samples for the control borings were taken at elevations corresponding to the elevations of samples taken under the landfill. The borings were made with a truck-mounted rotary drill using a hollow core 6-5/8-inch-O.D. flight auger. Soil samples were obtained by first drilling the hole with the flight auger to a depth slightly above that where the sample was to be taken. The internal drill rod was removed and either a 3-inch Hvorslev fixed-piston sampler fitted with a 3-inch-O.D. Shelby tube or a 1-3/8-inch split-spoon sampler lowered through the inside of the auger and pushed into the soil to obtain the sample. The Hvorslev sampler was used to obtain undisturbed soil samples and is illustrated in Figure 2. The split-spoon sampler was used when the soil would not remain in place in the Hvorslev sampler. A portion of the undisturbed soil samples was taken for chemical analysis and placed into airtight, acid-washed polyethylene jars. The jars were immediately packed in ice until time of analysis. A bailed sample of the groundwater from each boring was taken after the last soil sample was obtained, placed into airtight polyethylene jars, and immediately packed in ice until time of analysis.

The waste composing the landfill from each of the three trenches was sampled at 7 feet and at 20 feet, corresponding to the upper half of refuse thickness and at the soil-waste interface, respectively.

Following the completion of sampling, soil, groundwater, and waste samples were repacked in ice and shipped to the laboratory by air freight.

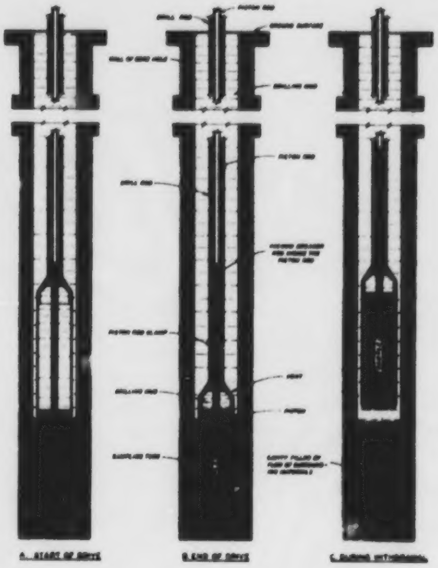

Figure 2. Hvorslev fixed-piston sampler and sampling procedure.

Preparation for Chemical Analysis

Upon arrival at the laboratory, the samples were placed in a 4°C cold room until time of extraction and subsequent chemical analysis. The time interval between sample acquisition and extraction-analysis was two weeks. The groundwater samples were centrifuged at 2200 rpm for 30 minutes. The supernate was then filtered through 0.45-μm millipore filters and preserved for chemical analysis as outlined in Table 1. Preservation methods and constituents to be analyzed are given in Table 1.

TABLE 1. PRESERVATION OF GROUNDWATER FILTRATES AND WATER EXTRACTS FOR CHEMICAL ANALYSIS

Preservative	Chemical Species
None	SO_4, SO_3, Cl, NO_3, NO_2
None	TOC
$HNO_3 + KMnO_4$ (pH 1)	Hg
HCl (pH 1)	Mg, Ca, Na, As, Be, Cd, Cr, Cu, Mn, Ni, Pb, Zn, B, Se
NaOH (pH 11)	CN

Water Extract

Two hundred grams of wet soil were weighed into 1000-ml polycarbonate centrifuge bottles, 800 ml distilled-deionized water added, the bottles sealed, and then shaken on a rotary shaker for 1 hour. Percent moisture was determined on a separate subsample of wet soil. After shaking, the bottles were centrifuged at 2200 rpm for 30 minutes and the supernate filtered through 0.45-µm millipore filters. The resulting extracts were preserved as outlined in Table 1 for chemical analysis. Results are reported as micrograms of constituent per gram of oven-dry soil.

HNO_3 Extract

Fifty grams of wet soil were weighed into 250-ml teflon beakers and 60 ml of 8N HNO_3 added. The soil-acid suspensions were heated to 95°C for 45 minutes and stirred every 15 minutes. After cooling to room temperature, the suspensions were quantitatively transferred and filtered with 8N HNO_3 through 0.45-µm millipore filters. The digested soil was washed three times with 20-ml portions of 8N HNO_3. The filtrate was quantitatively transferred with 8N HNO_3 to 250-ml volumetric flasks and made to volume, again using 8N HNO_3. The following elements were determined on the acid extracts: As, Be, Cd, Cr, Cu, Mn, Ni, Pb, Se, Zn, and B. Results are reported as micrograms of metal per gram of oven-dry soil (percent moisture was obtained from the distilled-deionized water analysis).

Chemical Analysis

Chemical analysis of the groundwater filtrates and water extracts listed in Table 1 was accomplished using the procedures and instrumentation as given in Table 2. It should be noted that the HNO_3 extracts were analyzed for only 11 of the 22 constituents indicated in Table 2.

This paper is a preliminary report for evaluation of a municipal sanitary landfill site concerning the pollution potential and vertical migration of contaminants; therefore, only five of the chemical contaminants outlined in Table 1 and Table 2 have been examined.

TABLE 2. PROCEDURES AND INSTRUMENTATION USED TO CHEMICALLY ANALYZE THE GROUNDWATER FILTRATES AND WATER EXTRACTS OBTAINED FROM SITE 01

Chemical species	Procedures and/or instrumentation
SO_4	Standard Turbidimetric Method* in combination with a Varian Model No. 635 UV-VIS Spectrophotometer
SO_3	Standard Potassium Iodite - Iodate Titration Procedure
Cl	Standard Mercuric Nitrate Titration Method*
NO_3, NO_2	Technicon II AutoAnalyzer, Industrial Method No. 100-70W**
TOC	Determined on an Envirotech Model No. DC 50 TOC Analyzer
Hg	Determined on a Nissei-sangyo Zieman Shift Atomic Absorption Spectrophotometer
+Mg, Ca, Na, As, Be, Cd, Cr, Cu, Mn, Ni, Pb, Zn, B, Se	Determined on an Argon Plasma Emission Spectrophotometer, Spectrametrics, Inc., Model No. II
CN	Technicon II AutoAnalyzer, Industrial Method No. 315-74W**

* Standard Methods for the Examination of Water and Wastewater, American Public Health Association, New York, Ed. 13, 1971.

** Technicon Industrial Systems, Terrytown, New York.

+ Only these metals were analyzed for in the HNO_3 extracts.

RESULTS AND DISCUSSION

Physical Analysis

Bulk density values ranged from 1.506 to 1.778 g/cc, averaging 1.645 g/cc. Water content values ranged from 2.4 to 7.5 percent and averaged 3.6 percent. Permeability of the soils ranged from 2.0×10^{-2} to 1.4×10^{-1} cm/sec with an average value of 0.91×10^{-1} cm/sec. The soil was classified as a sand to gravelly sand throughout the profile.

From the results of the physical data presented above, it can be concluded that the soil under the municipal landfill site 01 was extremely porous and should have little water-retention capacity. It should be expected, therefore, that given a high annual rainfall (50 inches per year) and the extreme porosity of the soil, leaching of contaminants from the municipal waste into the lower depths of the soil profile could occur.

Chemical Analysis

The curves in Figures 3 through 10 have been calculated in the following manner. The data points for the control curves represent the mean values of the chemical species obtained for boring 6 and boring 7A. The data points for the waste curves are the mean values of the chemical species obtained from borings 1, 2, and 3 taken directly under the landfill. Borings 6 and 7A were outside the landfill site, "updip" from the hydraulic gradient, and are therefore considered to represent control or background borings. The actual curves were calculated and plotted by fitting in a least squares sense the equation:

$$y = a + bx + cx^2 + dx^3$$

It should be pointed out that the r^2 values indicated on Figures 3-10 are not coefficients of determination but merely a goodness of fit of the data points to the third-order polynomial indicated above.

Chloride

The water extractable chloride (Cl) in micrograms of Cl per gram of soil was plotted against depth below the municipal waste-soil interface (Figure 3). Preliminary examination of the data indicated that Cl would be representative of the behavior of the water soluble chemical species considered in this study. As illustrated in Figure 3, Cl concentration was fairly constant with depth below the landfill and also below the control borings. The water extractable Cl concentration was near 20 µg/g from the municipal waste-soil interface through the soil column to a depth of 50 feet for both the waste and control. A slight increase, 2-5 µg/g, occurred below a depth of 50 feet below the landfill. Statistical analysis revealed no significant difference between the two curves. Chloride concentration in the groundwater was 5 µg/ml under both the landfill and the controls, indicating dilution had already occurred. The behavior of Cl, representing the soluble species, would indicate that after 15 years, most of the soluble species have been leached and have migrated from the upper depths of soil and from municipal waste through the soil into the groundwater. Due to the high soil permeability under site 01 and the high average rainfall, the leaching of the soluble species from the waste through the soil profile would be expected to occur.

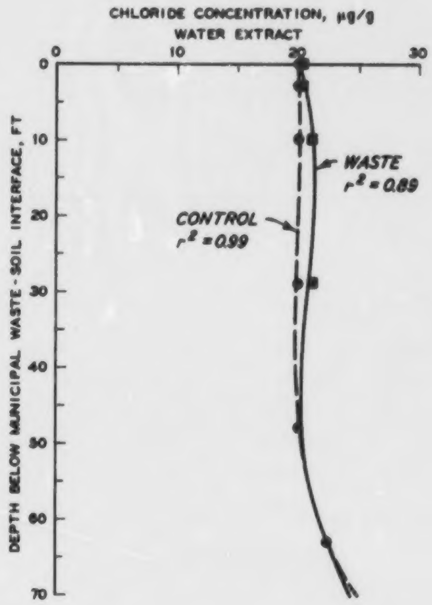

Figure 3. Chloride concentration in the soil under the waste and control borings as determined in water extracts.

Total Organic Carbon

The data in Figure 4 indicated that water extractable total organic carbon concentration (TOC) in the soil under the landfill was higher than that in the soil in the control borings. The TOC concentration at the municipal waste-soil interface was near 35 µg/g and indicated that TOC was still leaching from the waste some 15 years after the landfill had been closed. The shape of the TOC curve under the landfill (Figure 4) indicated that vertical migration of organic carbon had occurred. The concentration of TOC in the control borings from about 30 to near 60 feet below the landfill indicated that accumulation of organic carbon had occurred in the soil. The vertical migration of TOC under the landfill was further evidenced by the increased levels of TOC in the groundwater under the landfill versus the controls. The groundwater under the landfill had a higher TOC level, 39.7 µg/g, than that under the control, 23.5 µg/g. The data indicated that vertical migration of organic carbon through the soil column had occurred and had reached the groundwater under the landfill at site 01.

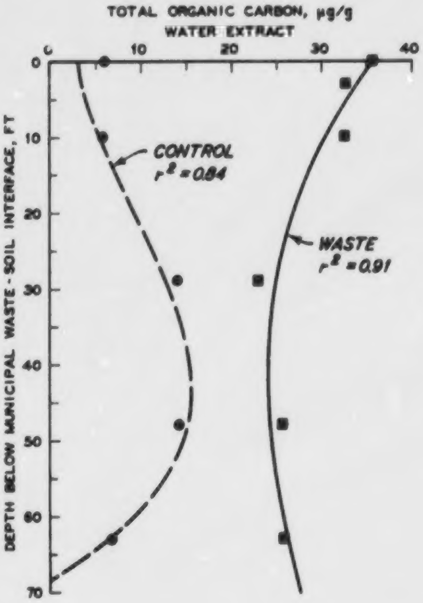

Figure 4. Total organic carbon in water extracts of soil under waste and control borings at site 01.

Chromium

Chromium (Cr) concentration in the nitric acid extract versus depth below the municipal waste-soil interface is shown in Figure 5. The data indicate that Cr behavior was different under the landfill when compared to Cr concentration in the control. The Cr concentration under the landfill remained fairly constant with depth, ranging from near 3 µg/g at the interface to slightly less than 2 µg/g immediately above the groundwater. Chromium concentration in the HNO_3 extracts of the control borings showed quite different behavior. Initial concentration was near 3 µg/g at the interface, increased to 5 µg/g at 15 feet, then decreased to 1-2 µg/g immediately above the groundwater. The different behavior of Cr in the HNO_3 extracts under the landfill and control borings indicated that

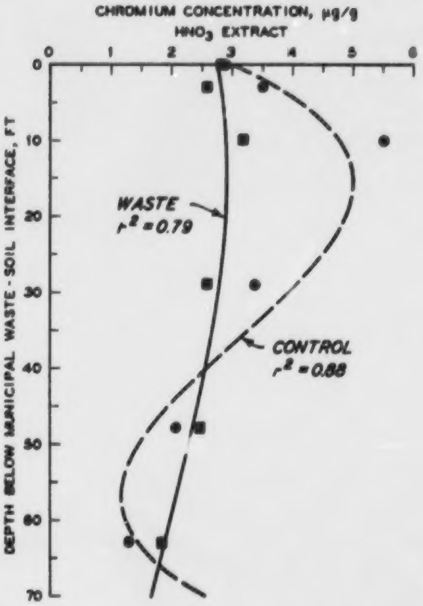

Figure 5. Chromium concentration in HNO_3 extracts of soil at site 01 under the waste and control borings.

vertical migration of Cr had occurred under the landfill. Evidently, some chemical component(s) leaching from the landfill was mobilizing soil Cr, resulting in decreased Cr in the soil under the landfill.

Chromium concentration in the water extracts versus depth below the municipal waste-soil interface is illustrated in Figure 6. The data indicated that there was virtually no difference in Cr concentration between the waste and control borings and that Cr concentration was constant (0.1 µg/g) throughout the soil profile from the interface to the groundwater. Solubility and movement of Cr from the soil beneath the waste apparently had already occurred. The data also indicated that either Cr had not reached the groundwater or that dilution had already occurred as there was no difference in concentration (0.025 µg/ml) between the waste and controls.

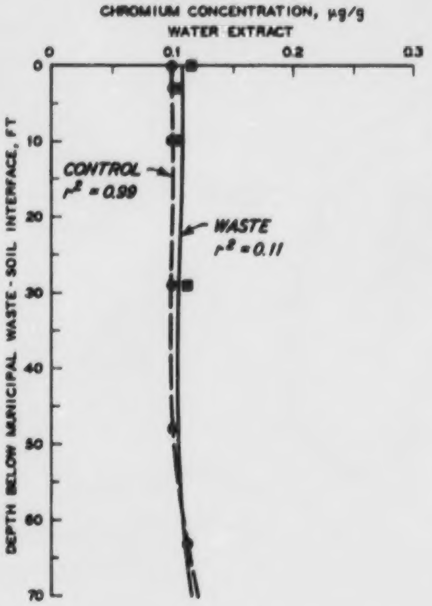

Figure 6. Chromium concentration in water extracts of soil at site 01 under the waste and control borings.

By comparing the data obtained in the water extract with those obtained in the acid extract, it is apparent that the water soluble Cr fraction was very low and fairly constant. Since the nitric acid extracts Cr from the organic fraction and part of the mineral fraction, apparently the vertical migration of Cr in the soil beneath the landfill had been affected by constituents contained in leachate from the municipal waste. As the leachates migrate vertically through the soil, they may form organic complexes with Cr which are soluble and together they migrate downward through the soil. Vertical migration of Cr proceeds until a point is reached such that the solubility of the proposed complexes is reduced resulting in attenuation.

Copper

The behavior of copper (Cu) in the nitric acid extract under the landfill (Figure 7) is similar to that of Cr in the nitric acid extract. In fact, the shape of the curves is almost identical. Again contamination of the groundwater by Cu was not indicated as the concentration of Cu was the same, 0.020 µg/ml, for both the control and the waste borings. This would seem to indicate that the same factors controlling vertical migration

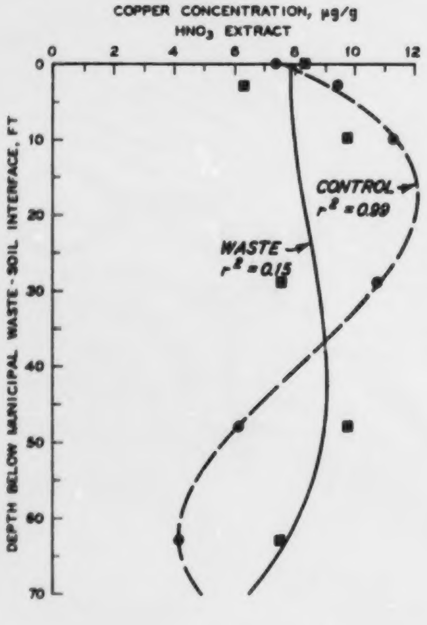

Figure 7. Copper concentration under the waste and control borings in HNO_3 extracts of soil at site 01.

and attenuation of Cr are also applicable to Cu. The same reasoning would hold true for Cu in the water extracts (Figure 8).

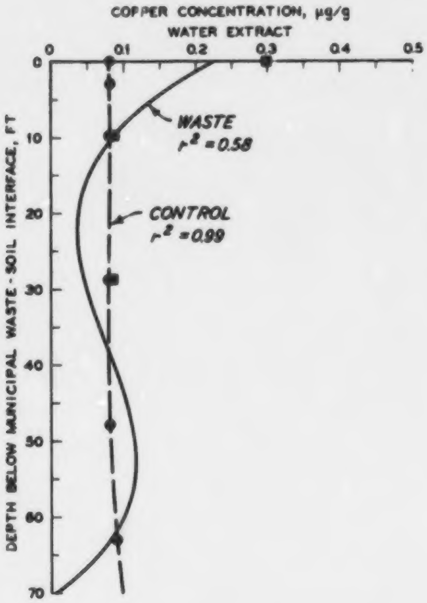

Figure 8. Copper concentration under the waste and control borings in water extracts of soil at site 01.

Cadmium

The vertical migration and attenuation of cadmium (Cd) in the soil beneath the landfill and control borings were somewhat different than the migration and attenuation of Cr and Cu and are illustrated in Figure 9 for the nitric acid extract and Figure 10 for the water extract. The concentration of Cd under the landfill was higher than that of the controls in both the acid and water extracts and was near 0.3 μg/g for both cases. The data in Figure 9 indicated that Cd concentration was somewhat higher under the landfill than under the control. The concentration of Cd in the water extract was very nearly equal to that in the nitric acid extract, especially under the landfill. The Cd concentration in the groundwater under the landfill was 0.05 μg/ml (mg/ℓ), while that under the control was 0.02 μg/ml. From the data presented for Cd, it can be concluded that the vertical migration of Cd

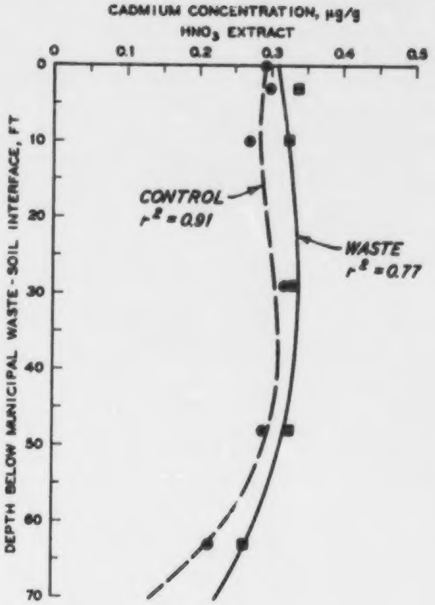

Figure 9. Cadmium concentration in HNO_3 extracts of soil at site 01 under the waste and control borings.

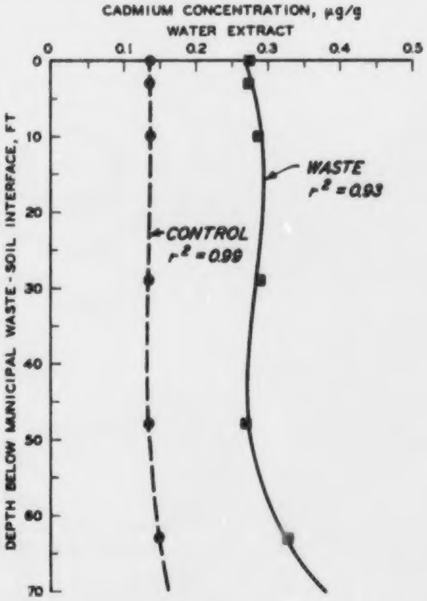

Figure 10. Cadmium concentration in water extracts of soil at site 01 under the waste and control borings.

through the soil profile is not affected by the leachate from the municipal waste to the extent that Cr and Cu are affected. Apparently, the proposed formation of Cd complexes with constituents contained in the leachate from the municipal refuse is more stable than the complexes of Cr and Cu. Assuming this to be true, one would expect Cd to migrate further down through the soil profile than either Cr or Cu.

Since it has been proposed that the mobility of Cr, Cu, and Cd was affected by some constituent(s) originating from municipal refuse, a regression analysis of TOC on the above metals was performed. Results of the regression analysis revealed, however, that little or no relationship existed between TOC and Cr, Cu, or Cd in either water or acid extracts. A possible explanation for the absence of a relationship between TOC and the metals is that the proposed organic complexes of Cr, Cu, and Cd are present in fraction(s) extracted in the acid digest (i.e. not water soluble). Since TOC was not determined on the acid extracts, little or no relationship between TOC in the water extracts and Cr, Cu, and Cd in the acid extracts should be expected.

CONCLUSIONS

From the results presented in this preliminary investigation of site 01, a municipal sanitary landfill, it appears that vertical migration and resultant contamination of groundwater occurred for the soluble chemical species as represented by the data presented for Cl. Vertical migration and resultant contamination by TOC and Cd originating from the landfill did occur. Vertical migration and groundwater contamination of Cr and Cu originating from the landfill did not occur.

The mobility and attenuation of Cr, Cu, and Cd are apparently affected by unknown constituents contained in the leachate from municipal refuse.

FIELD VERIFICATION OF HAZARDOUS INDUSTRIAL WASTE MIGRATION FROM LAND DISPOSAL SITES

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ABSTRACT

Development of effective investigative and monitoring techniques for detecting and quantitatively evaluating the extent of groundwater pollution from surficial toxic waste disposal sites in humid regions is the primary purpose of this study. It is also designed to verify in the field the effectiveness of soils and surface deposits in a glaciated region to retain specific hazardous chemicals. Three study sites were selected on the basis of geology, types and quantities of hazardous wastes, and manner of waste disposal. These sites are underlain by low-permeability silts and clays that should be efficient in retaining the toxic wastes and minimizing groundwater pollution. An extensive drilling program to obtain unconsolidated sediment cores and groundwater samples for chemical analyses has been undertaken at each site. This paper describes methodologies used and preliminary results at one of the three sites. Work to date shows that soil coring is an effective tool for mapping the migration patterns of chemical pollutants through the earth materials. This approach also provides field data to verify the effectiveness of various soil types to adsorb or retain different chemical pollutants.

INTRODUCTION

In Illinois, 62 land disposal sites are permitted by the State Environmental Protection Agency to receive hazardous chemical wastes. In addition, more than 1000 active or abandoned landfill sites and several hundred private industrial disposal sites have received large but unknown quantities of all types of wastes including toxic chemicals. Many of these are adjacent to or directly underlain by shallow aquifer systems vulnerable to pollution from surficial sources.

The amount and areal extent of hazardous material migration from these disposal sites in Illinois is not known. Few sites are monitored for possible pollution of contiguous aquifers and those that are monitored appear to be ineffectively instrumented. Traditionally, monitoring wells are installed and water samples collected and analyzed periodically. However, these wells generally cannot monitor very large vertical segments of an aquifer, and the water samples are not always analyzed for the many different organic or inorganic chemical compounds that may originate from the disposal sites.

Existing air and surface-water pollution regulations are forcing an ever-increasing volume of hazardous chemical waste to the land for ultimate disposal. This is true particularly in the heavily populated and industrialized regions of the United States where most of these wastes are generated, used, and eventually discarded. In the humid parts of the country, shallow groundwater reservoirs are recharged by precipitation infiltrating through the land surface. As a result, many shallow aquifers may be in danger of serious water quality degradation if soils are not effective in keeping hazardous wastes from migrating downward to the aquifers. Knowledge of groundwater pollution occurrences from such sources is steadily increasing. These occurrences indicate that a serious threat to public health may exist until all surface and underground toxic chemical disposal sites are located, any migration or groundwater pollution evaluated, and corrective measures applied where necessary.

Purpose of Study

The primary purpose of this study is to develop effective investigative and monitoring techniques for detecting and evaluating quantitatively the extent of groundwater pollution from surface toxic waste disposal sites. The study also is designed to verify in the field the effectiveness of glaciated region soils and associated surface deposits in retaining specific hazardous chemicals.

The findings of this study should provide an invaluable tool for predicting possible long-term effects of hazardous chemical disposal on land. Also, the methodologies used should be immediately applicable in evaluating the extent of hazardous chemicals migration from disposal sites situated in similar geohydrologic environments throughout Illinois and much of the other 15 glaciated, humid-region states in the country.

SITE SELECTION

Three sites were selected for study on the basis of geology, the types and quantities of hazardous wastes generated, and the manner of waste disposal. Sites were selected where the unconsolidated materials range from about 15 to 75 feet thick and consist predominantly of low-permeability silt and clay soils. Pennsylvanian age shales or sandstones also lie beneath the glacial deposits at all three sites. Thus, from the geology, these sites would theoretically be desirable disposal areas with little resulting groundwater pollution.

Two sites (A and B) are secondary zinc smelting plants located in south-central Illinois. A large quantity of waste from these plants has been disposed of in solid form on the plant property over several years of operation. The other site (C) is a chlorinated hydrocarbon processing plant located in east-central Illinois. Approximately half of the liquid waste from this plant is stored and pretreated in lagoons or pits on the plant property and then injected into a deep disposal well. The possible effects of the surface lagooning and storage pits are the principal concern in this study. This discussion will be limited to work accomplished at Site A.

Site A

Site A is a secondary zinc smelter located in south-central Illinois. The plant, which started operations between 1885 and 1890, initially processed zinc ore. It was converted to a secondary zinc smelting facility about 1915. Wastes from the smelting operations during the first 85 years were principally heavy metals-rich cinders, and ashes. During the early years large quantities of cinders were used as road fill or surfacing for secondary roads and farm lanes in the plant area. The remainder was used as fill material around the plant buildings and as surfacing over the property. As a result of these disposal practices, there now is a 1- to 10-foot thick layer of metals-rich cinders covering about 12 acres of the plant property.

In compliance with air pollution control regulations, a scrubber was installed on the plant stack in 1970. Prior to that time, wind-blown ash, rich in zinc and other heavy metals, was deposited on the plant site and on approximately 100 acres of surrounding farmland. This source of pollution has now been minimized, but wastewater from the scrubber (about 14,500 gallons per day) is deposited in a seepage pit constructed on the cinder materials that form the land surface at the site. Several hundred tons of high zinc content sludge have accumulated from the frequent cleaning of this pit and are now being reprocessed for zinc and lead recovery. Most of the water from the pit infiltrates into the ground underlying the plant property.

Prior to the study, limited data suggested that groundwater pollution might be occurring from three possible sources:
1) the large volume of solid waste material (cinders and stored junk to be processed) at the plant site; 2) highly mineralized liquid wastes from the stack scrubbers; and 3) wind-blown ash from the smelter furnaces prior to installation of the scrubbers.

Because of the long period of operation of this facility and the various sources and forms of pollution likely to be present, this site appeared to be most desirable to study in detail. The decision was made to devote maximum time, effort, and money at this site to develop the study methodology and optimize its application to other sites.

METHOD OF INVESTIGATION

An extensive drilling program to obtain unconsolidated sediment cores and groundwater samples has been undertaken at each site. Chemical analyses of the core and groundwater samples are being used to define: 1) the vertical and horizontal migration patterns of chemical pollutants through the shallow glacial deposits and aquifer profiles; 2) the seasonal variation of toxic chemical levels in groundwater near these sites; and 3) the residual toxic chemical buildup in the unconsolidated materials in the vicinity of the sites.

Coring

Continuous vertical core samples for geologic study and chemical analyses have been obtained with conventional Shelby tube and split spoon sampling methods through hollow stem augers. These dry drilling techniques were used to minimize chemical alteration of samples from drilling fluids or external water during excavation.

Coring has been done with a truck-mounted Central Mining Equipment (CME) 55 and a CME 750 rig mounted on an all-terrain vehicle. The drilling crew consisted of an equipment operator and helper, assisted if necessary by the principal investigators. For the first few test holes drilled at each site, a geologist from the State Geological Survey assisted in collecting samples and made preliminary soil identifications for use in subsequent testing.

Shelby tube and split spoon samples were extruded in the field as collected, cut into 6-inch lengths, placed in properly labeled wide mouth glass jars, and delivered to the State Geological Survey and Environmental Analytical Research Laboratory at the University of Illinois for processing and analyses. One 6-inch length of core from each 5-foot segment and/or change in formation was taken by the drilling contractor for moisture content determinations before being sent for geological and chemical analyses.

Core Analysis

Core samples for heavy metals determinations are being analyzed at the Environmental Analytical Research Laboratory with zinc as a target element. Previous experience in determining heavy metal contaminants in soil showed that digestion of a dried soil sample in 3 $\underline{N}$ HCl at slightly elevated temperatures effectively releases the heavy metals without destructing the silicate lattice of the soil. The heavy metals so released are determined by atomic absorption spectroscopy, the principal methodology used to date.

For a limited number of soil samples, the multi-element capability of optical emission spectroscopy has been used to determine the Cd, Cu, Pb, and Zn concentrations. Now, instrumentation and methods are being developed for use of nondispersive X-ray emission spectroscopy to permit semi-automated multi-element analysis for a larger number of elements with greater efficiency than is possible with current methods.

Preliminary tests using atomic absorption measurement of small spot samples indicate that the 6-inch long samples are too heterogeneous to permit reproducible analysis. Reproducible results have been attained by homogenizing the samples and subdividing them to sample weight levels of 1 gram for atomic absorption and 50 milligrams for emission spectroscopy. Pelletized samples of approximately 2 grams have been prepared for X-ray emission spectroscopy.

Well Construction

Analyses of water samples from observation wells has been the traditional method for monitoring groundwater pollution. To demonstrate the effectiveness of such an approach and the relative cost of using wells as compared to coring, a number of small-diameter (2-inch) observation wells were constructed. At Site A, where heavy metal contaminants were expected, plastic casing, screen, and pumping equipment were used.

Observation wells at Site A were constructed in the following manner. A 7-inch diameter hole was constructed and a 2-inch diameter PVC pipe (bottom 2 feet slotted with a hacksaw) was placed in the hole. Gravel was placed from the bottom of the hole to a level about 1 foot above the slotted portion of the pipe followed by about 6 inches of sand. The remainder of the annulus was filled with bentonite slurry to land surface (see Figure 1). A shallow well (10-15 feet deep) was constructed at each location (see Figure 2) and deeper

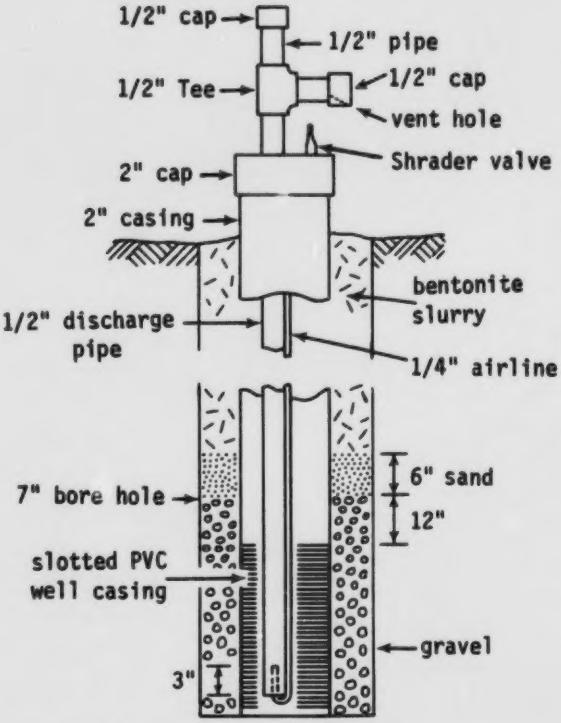

Figure 1. Typical well and pumping mechanism.

wells just above the bedrock were added at nine locations.

Observation wells are equipped with individual pumping devices to minimize possible contamination of well samples from other wells. The pumping device consists of a 1/2-inch diameter PVC discharge pipe that extends from above the 2-inch well casing to the bottom of the well. A tee fitted with short nipples and removable caps is placed at the top of this pipe (Figure 1). The cap on the vertical segment can be removed to allow for water level measurements within the 1/2-inch pipe. The cap on the horizontal segment (water discharge outlet) is vented to permit stabilization of the water level within this pipe.

A 1/4-inch plastic airline also is installed in each well. The airline is attached to a Shrader valve at the top of the well casing and extends the entire depth of the well. The lower end of the airline is bent up into the bottom of the 1/2-inch discharge pipe for a distance of about 3 inches. Water is pumped from the wells by removing the cap from the horizontal portion of the 1/2-inch pipe and applying air to the system through the Shrader valve. Pumping from depths as great as 70 feet is possible with only a bicycle-type hand pump. A gasoline powered 4-cylinder air-compressor capable of delivering about 5 cubic feet per minute at pressures up to 60 psi is being used. An activated charcoal filter has been placed in the discharge line from the compressor to insure that air from the compressor is not introducing airborne contaminants.

Water Sample Analysis

Water level measurements are made and water samples collected from each well once a month. Samples are collected in 6-ounce plastic containers and placed on ice until they can be refrigerated in the laboratory. Each well is pumped for a period adequate to insure that all stored water in the well casing has been removed. The wells are allowed to recover and a sample is then collected from the water that has just entered the well. This procedure insures that the water sample collected is representative of the water flowing through the aquifer at the time of collection.

Heavy metals are determined by atomic absorption spectroscopy with appropriate correction for blank and background absorption. Concentrations of Zn, Pb, or Cu below the detection limit of atomic absorption spectroscopy are determined by anodic stripping voltammetry.

Secondary Methods

A number of qualitative methods of groundwater pollution detection and mapping have been used with varying degrees of success. In an effort to evaluate the relative effectiveness of a few of these methods, electrical earth resistivity surveys, soil temperature surveys, soil and vegetation mapping, and color-thermal infrared and normal color photography have been employed at Site A.

RESULTS

To date, 47 wells at 34 locations have been completed at Site A. Cores were taken at each well and at 19 additional sites (Figure 2). Total well and core sampling

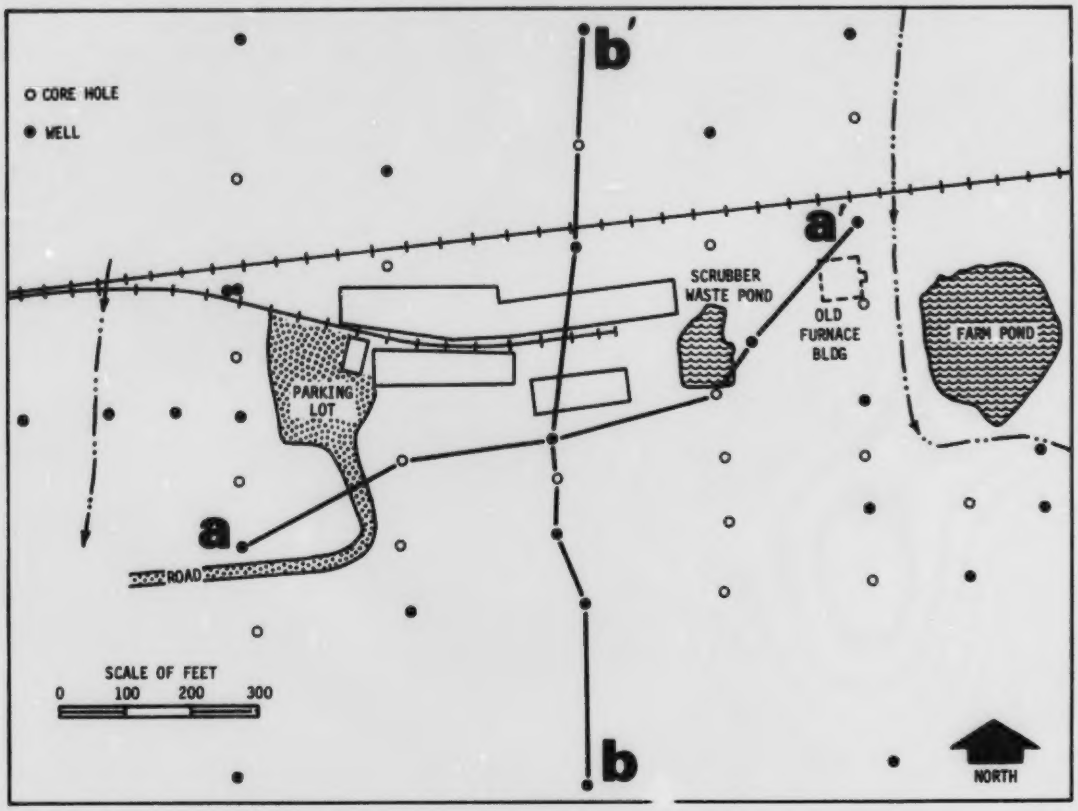

Figure 2. Location map of central portion of Site A.

footages are about 1300 and 1275 feet respectively.

The glacial materials at this site are about 60 to 75 feet thick. The stratigraphic units recognized are essentially uniform in character and thickness and generally flat. The elevation of the surface of the Pennsylvanian bedrock dips from 447 feet above sea level on the east to about 432 feet on the west. A brief description of the units, from top down, follows:

A) Peoria Loess (4-6') - Brownish gray clayey silt, noncalcareous, with iron stains.

B) Roxana Silt (3-4') - Dark brown clayey silt with up to 34% sand (av. 20%), noncalcareous.

Glasford Formation

C) Berry Clay Member (3-4') - Dark gray sandy silty clay with trace gravel, up to 40% sand, noncalcareous (an accretion gley).

D,E) Vandalia Till Member (2-8') - Yellowish brown, oxidized in upper portion, little yellowish gray at base, sandy silt, slightly gravelly, calcareous; thin silty sand (D) at top (1/2-1 1/2') appears continuous across area; upper 14-18' of till below, although less sandy, may be part of Vandalia.

F) Smithboro Till Member (25-31') - Dark gray sandy silt till, with little gravel, contains discontinuous lenses of silt, sand and dark olive brown, leached silty clay, probably sheared into the Smithboro from the Lierle Clay below, generally tough, compact, generally calcareous but carbonate content less in lower 18'. This unit may be divided into an upper and lower zone separated by a silt bed. No conclusion has yet been drawn concerning the relationship of units E and F.

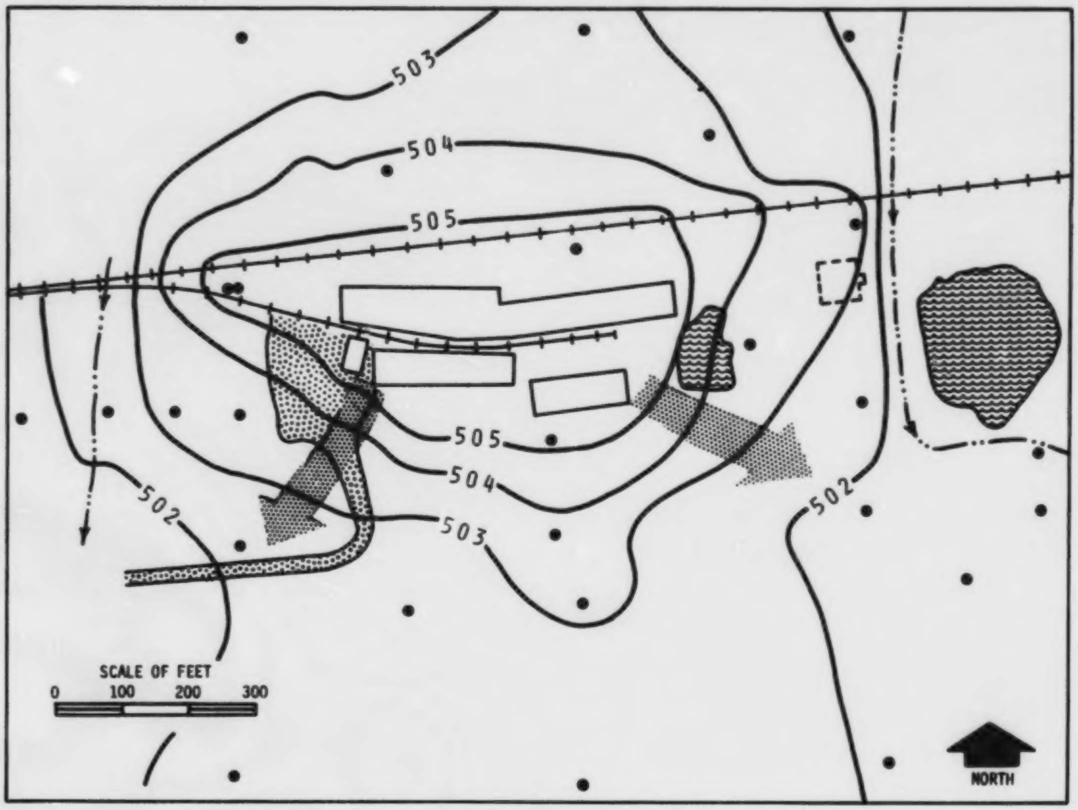

Figure 3. Water table contour map, Site A (November 1975).

G) Lierle Clay Member (1-2') - Dark olive brown sandy silty clay, with little gravel, noncalcareous, soft.

Banner Formation

H) Unnamed Till Member (1-2') - Gray clayey silty till, sandy, with some gravel, mottled yellowish brown, brown and gray in upper part, strongly calcareous, hard, dry, a few scattered silt and sand lenses, predominantly dry.

Bond Formation (Pennsylvanian bedrock) - Greenish gray shale with abundant mica: hard, dry.

The stratigraphic units and the textural mineralogical data are shown in Table 1. The expandable clay minerals, generally referred to as montmorillonite (M), make up more than 80% of the clay minerals within the Peoria Loess, Roxana Silt, and Berry Clay Member, thereby suggesting a high base exchange potential in the upper 13 feet of the materials encountered. The thin, continuous silty sand zone at the top of the Vandalia Till would appear to be the only 'permeable' unit to allow groundwater to travel laterally at any moderate rate away from the site. Although there is probably some downward movement of groundwater through the remainder of the Glasford Formation, it would be expected to be extremely slow.

Water level measurements taken in the shallow wells were used to construct monthly water table contour maps for the te. These wells are from 10 to 15 feet below land surface and are all finished in the sandy unit (D) at the top of the Vandalia Till Member. Data collected to date show no significant change in the shallow water levels at this site. The principal groundwater flow paths from the plant site are illustrated in Figure 3. Water from the eastern half of the plant, including the liquid disposal pond, appears to be moving east-southeast; water from the western half of the plant site seems to be moving west-southwest. Therefore, any pollutants in

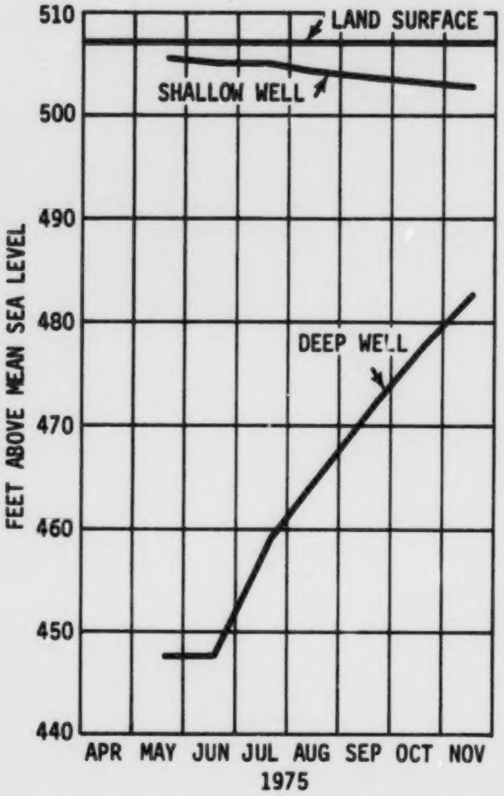

Figure 4. Water level elevations.

TABLE 1. TEXTURAL AND MINERALOGICAL DATA

Units	Thick-ness (ft)	% Sd	% St	% Cl	% M in Cl	Total % M
(A) Peoria Loess	4-6	3	58	39	86	33
(B) Roxana Silt	3-4	20	49	31	91	28
(C) Berry Clay	3-4	28	28	44	87	38
(D) Vandalia Till	.5-1.5	51	31	18	38	7
(E)	2-8	34	35	31	28	9
(F) Smithboro Till	25-31	29	42	29	53	15
(G) Lierle Clay	1-2	21	40	39	71	28
(H) Banner	1-2	28	41	31	56	17

Sd = sand, St = silt, Cl = clay,
M = montmorillonite

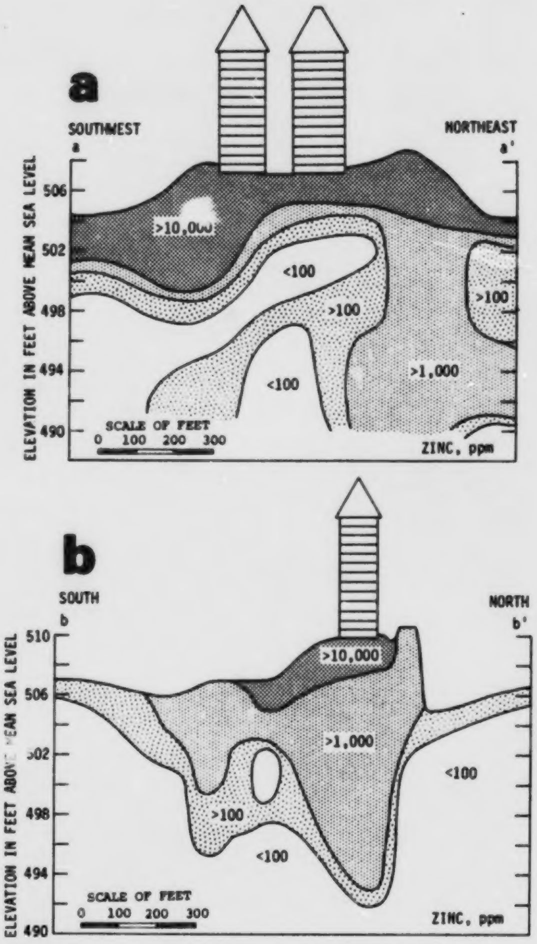
a
SOUTHWEST
a
NORTHEAST
a'
ELEVATION IN FEET ABOVE MEAN SEA LEVEL
506
502
498
494
490
>10,000
<100
>100
>100
<100
>1,000
SCALE OF FEET
0 100 200 300
ZINC, ppm
b
SOUTH
b
NORTH
b'
ELEVATION IN FEET ABOVE MEAN SEA LEVEL
510
506
502
498
494
490
>10,000
>1,000
<100
>100
<100
SCALE OF FEET
0 100 200 300
ZINC, ppm

Figure 5. Soil zinc concentrations.

the shallow groundwater system should be moving in the same general directions.

No piezometric surface maps have been prepared for the deeper units at this site. Measurements in the wells indicate that water levels have not stabilized even after 5 to 6 months of nonpumping (Figure 4). This is due to the low permeability of the unit (Banner Formation) in which these wells are finished.

Single element analyses for zinc have been completed on samples from most of the core holes at this site. Figure 5 illustrates zinc concentrations in the soil along two vertical cross sections through the study area. An explanation of the physical and chemical phenomena controlling the movement of zinc into the soil cannot be made until multi-element chemical analyses and textural and mineralogical data are available for all soil samples.

From general observations, it is noted that the higher zinc concentrations in soil are limited to the areas directly beneath the cinder fill covering the plant property. The deepest vertical penetrations also seem to lie beneath the areas of thicker cinder fill and prefill topographic depressions.

Analyses of water samples from the wells at this site are now in progress. In general, zinc concentrations of water from all wells are less than 1 ppm and do not appear to vary significantly from month to month. Preliminary data also suggest that mineral concentrations in the samples stabilize after the second or third month of sampling.

Complete analysis of all soil and water samples should provide the needed data to explain the phenomena controlling the movement of heavy metals from this site.

Preliminary Cost Analysis

As previously stated, it was decided at the beginning of this project to devote maximum time, effort, and money at Site A to gain the needed experience and understanding of the methodologies being applied. Therefore, the total expenditures at this site are much higher than would be necessary at other sites of this type. The cost to study a similar site using a minimum monitoring approach would be considerably less.

As of January 1, 1976, approximately 1275 linear feet of piezometer-tube observation wells at 34 different locations have been completed at a total cost of about \$6150 (\$4.80/foot). Approximately 1300 linear feet of coring has been done for about \$9150 (\$7.05/foot).

As time permits and we gain better understanding of the monitoring methods being tested, the cost effectiveness of the coring technique combined with a minimum number of wells will be determined. Preliminary data suggest that soil coring is the more reliable monitoring technique and definitely should be used to locate the proper vertical horizons for installing monitoring wells.

SUMMARY

Work completed at all 3 sites to date has demonstrated that soil coring is an effective tool for mapping the migration patterns of chemical pollutants through the earth materials. This approach also provides field data to verify the effectiveness of various soil types to adsorb or retain different chemical pollutants.

The 3 sites investigated have been in predominantly dense silt and clay environments. To determine the general applicability of the coring technique to other types of environments, it is planned to conduct an abbreviated pilot study at a zinc smelter located in a sandy river bottomland area.

Sufficient comparative data are not available at this time to determine the relative usefulness of the supplemental methods being tested in this study. Temperature surveys, electrical earth resistivity surveys, and vegetation mapping and sampling may prove to be useful in certain shallow geologic regimes. Although color infrared photography is very limited in detecting groundwater pollution, it is a useful tool for soil and vegetation mapping and for detecting surface water pollution.

ACKNOWLEDGMENTS

This study is sponsored by the Solid and Hazardous Waste Research Division of the Federal Environmental Protection Agency (Grant R/803216-01) under the general guidance of Mike Roulier, Project Officer. Special thanks are given to Dr. Keros Cartwright of the Illinois State Geological Survey and Dr. Arnold Hartley of the Environmental Research Analytical Laboratory for their enthusiastic cooperation in this study. Thanks also are due W. H. Walker, Geraghty & Miller, Inc., who conceived and initiated the project before leaving the Illinois State Water Survey.

EVALUATION OF SELECTED LINERS WHEN EXPOSED TO HAZARDOUS WASTES

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ABSTRACT

Disposal or impoundment of hazardous wastes on land presents the potential of these wastes, or leachates of the wastes, seeping into the ground and polluting surface and ground water. The use of impervious barriers to intercept and control this seepage offers a means of reducing and possibly eliminating such pollution. An experimental research project is now underway to assess the relative effectiveness and durability of a wide variety of liner materials exposed to hazardous wastes. The materials under study include soils and clays, soil cements, asphaltic concretes and other asphaltic compositions, and a wide range of polymeric membranes. The polymeric materials used in the manufacture of these membranes include polyvinyl chloride, chlorinated polyethylene, chlorosulfonated polyethylene, ethylene propylene rubber, neoprene, butyl rubber, an elasticized polyolefin, a thermoplastic polyester, and polyurethanes. In this study the liner materials are being exposed to such hazardous wastes as strong acids, strong bases, oil refinery tank bottom wastes, lead wastes from gasoline, saturated and unsaturated hydrocarbon wastes, and a pesticide. The experimental procedure being followed is described and results of preliminary tests used in the selection of materials for extensive testing are presented.

INTRODUCTION

Our highly industrialized society produces a great range of nonradioactive industrial hazardous and toxic wastes in the manufacture of materials and products. The need for improving the methods of handling, storing, and disposing of these wastes is becoming more apparent (1-4). In passing the Resource Recovery Act of 1970, Congress perceived the hazardous waste storage and disposal to be a problem of national concern (1). They mandated the Department of Health, Education and Welfare, later the Environmental Protection Agency, to prepare a comprehensive report and plan regarding the storage and disposal of hazardous waste including an identification of the hazardous waste streams which should require special handling.

In their "Report to Congress on Hazardous Waste Disposal" (1), EPA concluded that the current management of the nation's hazardous residues is "generally inadequate" and that the "public health and welfare are being unnecessarily threatened by the uncontrolled discharge of such waste materials into the environment". In this report it is pointed out that approximately 10 million tons of nonradioactive hazardous wastes are being generated per year and of these 60% are organic and 40% inorganic. Of these wastes 90% occur in liquid or semiliquid form. Generation of these hazardous wastes is growing at the rate of 5-10% per year. Disposal on land is increasing even faster as a result of air and water pollution controls which deny air and water as disposal sites and require the converting of such wastes into solid or semisolid form which must be disposed of on land. Furthermore, ocean-dumping is becoming unacceptable for many wastes. This increased disposal of hazardous wastes on land requires greater need to prevent toxic materials from entering and polluting ground water systems.

Confining hazardous wastes in pits, ponds, lagoons, landfills or other storage areas lined with impermeable barrier materials is being considered as a means of storing hazardous wastes, even after treatment to detoxify them. Accordingly, this project was set up to assess the performance of various recognized liner materials when exposed to hazardous wastes, to determine the state of technology, and to supply information which would be realistic and useful in establishing regulatory controls which the EPA recommended (1) to insure adequate management of the collection, storage, and disposal of hazardous wastes.

This paper is a progress report of the experimental work now underway on EPA Contract 68-03-2173 to make this assessment of liner materials. The overall approach is described, the experimental plan outlined, and exploratory results which were obtained in selecting materials for intensive testing are presented.

BACKGROUND

Potential Impermeable Barriers

A wide range of materials are potentially useful as barriers for impounding hazardous liquids and sludges (5-9). Many are currently being used to line ponds, reservoirs, lagoons, and canals for the purpose of reducing or eliminating the loss or seepage of liquids into the ground. These liners vary considerably in permeability, durability, and cost. Selection of a liner for a given installation depends upon soil conditions, availability of materials, the level of performance required, and the design of the pond. Some of the materials which have been used as pond liners or impermeable barriers, or appear to be good candidates for such applications, are presented in Table I.

Compacted soils, clays, soil cements, and asphaltic materials have found wide use for lining ponds, etc.; nevertheless, they have limitations particularly in respect to their permeability to different fluids.

The synthetic polymeric membranes are of particular interest because of their low permeability. However, they can vary considerably in physical and chemical properties, installation, overall performance, and costs. In addition, even for a given polymer, there can be considerable variation in the liners among different manufacturers due to compound and design differences.

TABLE I. MATERIALS POTENTIALLY USEFUL FOR LINERS OF PONDS CONTAINING HAZARDOUS WASTES.

Compacted native fine-grain soils.

Bentonite and other clay sealants.

Asphaltic compositions:
- Asphalt concrete
- Hydraulic asphalt concrete
- Preformed asphalt panels
- Catalytically blown asphalt sprayed on soil
- Emulsified asphalt sprayed on soil or on fabric matting
- Soil asphalt
- Asphaltic seals

Portland cement compositions:
- Concrete, with seal coats
- Soil cement, with and without seal coats

Soil sealants:
- Chemical
- Lime
- Penetrating polymeric emulsions and latexes

Sprayable liquid rubbers:
- Polyurethanes
- Polymeric latexes

Synthetic polymeric membranes - reinforced and unreinforced:
- Butyl rubber
- Ethylene propylene rubber (EPDM)
- Chlorosulfonated polyethylene (Hypalon)
- Chlorinated polyethylene (CPE)
- Elasticized polyolefin (3110)
- Polybutylene (PB)
- Polychloroprene (Neoprene)
- Polyester elastomers
- Polyethylene (PE)
- Polyvinyl chloride (PVC)

Factors In Selecting Liners for Specific Installations

In selecting liner materials for confining hazardous wastes some of the factors which must be considered are:

- "Compatibility" of the liner material with the particular hazardous waste to be confined. For example, many wastes will contain organic materials even in small amounts which can swell or deteriorate a liner or damage the seams. Such liners as butyl, EPDM and asphalt would probably be damaged by wastes containing hydrocarbons. Also, some impermeable soils can lose their impermeability when impounding strong acids, bases or brines. Some can be seriously affected by increased temperatures.

- The level of permeability allowable for a given waste. At times very low permeability is required.
- Lifetime required and the level of impermeability needed over a period of time.
- Whether the liner will be exposed to sunlight and weather. Some of the liner materials, such as soils, can lose impermeability due to freeze-thaw and drying or by wave action of the liquid being impounded. Synthetic membrane films, such as polyvinyl chlorides, can become excessively brittle either due to loss of plasticizer by evaporation or due to polymer degradation resulting from ultraviolet light. Butyl can crack because of ozone on extended exposure.

Specific materials for exposure in this test program were selected on the basis of these factors.

OBJECTIVES OF PROJECT

- To determine the effects of exposure to various wastes upon the physical properties, particularly the permeability, of liner materials over a period of 24 months.
- To estimate the effective lives of twelve liner materials exposed to six types of nonradioactive hazardous waste streams generated by industry under conditions which simulate those encountered in holding ponds, lagoons, and landfills.
- To develop the information needed for recommending different lining materials for confining hazardous wastes.
- To determine the durability and cost effectiveness of the various liners for confining different hazardous wastes.
- To develop a method for assessing the relative merit of the various liner materials for specific applications and for determining service lives.

EXPERIMENTAL PROGRAM

In our overall experimental program, we shall:

- Expose liner specimens of about one square foot area, with seams, sealed in the bottom of cells containing approximately one foot of waste above the specimen.
- Measure the seepage of the waste through the liner and determine the effect on properties of the liners over a two-year period.
- Perform exploratory tests of liners and wastes to determine their "compatibility" and suitability for long-term exposure tests.
- Determine the effects on the properties of a wide range of liner materials immersed in wastes.
- Expose specimens of the liners to the weather, observe and measure changes in properties.
- Expose samples of selected liners to the weather and wastes simultaneously by placing in partially filled troughs.
- Fully characterize each of the hazardous wastes.

The main effort in this project will be the exposing of selected liner specimens in the one cubic foot cells and determining the effects of the exposure upon the liners and their performance. A schematic drawing of the cells is shown in Figures 1 and 2. The cell shown in Figure 1 is for the polymeric membrane liners with a seam; that shown in Figure 2 is for the admix liner specimens which are thicker and must be mounted in a spacer between the base and the tank containing the waste. These cells are fabricated from steel and coated with a chemically resistant epoxy coating. The base of the cell is filled with a chemically inert high quality silica in order to prevent reactions of the waste which may seep through the liner. These cells will be disassembled after one and two years exposure and the liners recovered and tested. The cells, 144 in all, are placed on a rack at the Richmond Field Station of the University of California, Berkeley.

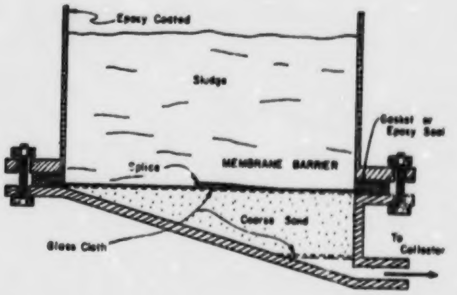

Figure 1. Schematic drawing of exposure cell for membrane liners. Exposed area of liner is 10" x 13" and depth of the waste is one foot.

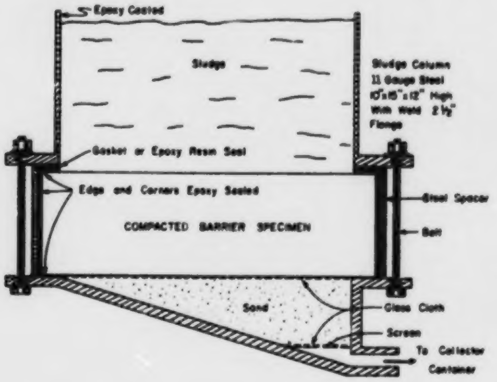

Figure 2. Schematic drawing of exposure cell for admix liners. Exposed area of liner is *ca* 12" x 15" and depth of the waste is one foot.

After obtaining the wastes, it was recognized that several of the liners would not withstand exposure to certain wastes and, thus, some combinations were eliminated from the long-term testing. A series of exploratory experiments were run to determine which combinations should be tested. These exploratory tests were of three types:

- Immersing 1" x 6" strips of the membrane liners in the wastes in one-gallon containers and observing the effects, e.g. swell, over a period of several weeks.

- Mixing modified bentonites with sand in a ratio of 1 to 4 parts by weight and placing a one-inch layer in the bottom of perforated 400 ml polyethylene beakers, soaking for one week, and then pouring two inches of hazardous wastes on top and observing seepage through the liners.

- Sealing permeability test specimens of asphalt concrete, soils, and soil cement in two-inch glass tubing, placing two inches of strongly acidic and basic hazardous wastes above them, and observing seepage through the respective liners.

As we have a large number of different liner materials, but could only test a limited number mounted in the bases of the cells, it was felt that a wider study of the other materials could be performed by immersing specimens in the waste tanks which are part of the exposure cells. These specimens will be hung in the wastes and removed at various times to have their physical properties determined.

Many liners for ponds are exposed to the weather and sunlight. In some cases, it is necessary to cover these liners to avoid the degrading effects of wind and sunlight. Consequently, we plan to expose samples on roof-aging racks in Oakland to sunlight and weather and determine the effects on the properties. In addition, the effect of raising and lowering the level of a pond may cause degradation at the water line. We, therefore, plan to expose selected liners in troughs in which both sunlight and wastes can interact with the liner material.

We recognize that only a limited number of wastes can be used in these tests. In order to give the data some broad usefulness, we shall characterize the wastes fully. This characterization will be performed by the Sanitary Engineering Research Laboratory of the University of California at Berkeley. We believe that extrapolations can be made to a wide range of hazardous wastes by using the experience obtained on the highly characterized wastes.

As the ultimate failure of a liner will be when it no longer holds the waste which it is impounding, observation of the seepage of the waste through the liners will be made and the wastes will be analyzed. It is expected that most of the liners will not allow seepage within the two-year period. In order to make estimates of the service life of these materials, the normal physical properties will be measured as a function of time. It is felt that some of the tests will correlate with liner performance and service life. The tests which will be run on the polymeric membrane liners are shown in Table II; tests for the admix materials are shown in Table III.

TABLE II. TESTING OF POLYMERIC MEMBRANE LINERS.

Water permeability - ASTM E96.

Thickness.

Tensile strength and elongation at break, ASTM D412.

Hardness, ASTM D2240.

Tear strength, ASTM D624, Die C.

Creep, ASTM D674

Water absorption or extraction at RT and 70°C, ASTM D570.

Seam strength, in peel and in shear, ASTM D413.

Puncture resistance - Fed. Test Method Std. No. 101B, Method 2065.

Density, ash, extractables.

TABLE III. TESTING OF ADMIX LINER MATERIALS.

Water permeability - Back pressure permeameter (10).

Density and voids - ASTM D1184 and D2041.

Water swell - Calif. Div. of Hwys 305.

Compressive strength - ASTM D1074.

Viscosity, sliding plate of asphalts - Calif. Div. of Highways 348.

PROGRESS OF WORK AND PRELIMINARY REPORT

Selection of Liners for Exposure

After reviewing the available liner materials, five admix type and eight specific polymeric membrane materials were selected for exposure testing as liners in the cells. These materials are listed in Table IV.

The admix liners were selected or designed to yield permeability coefficients of 10^{-7} cm/sec or less. In the case of the soil cements and compacted fine-grain soils, a variety of compositions was compacted in order to achieve the desired coefficient of permeability. An extended search was made for native fine-grain soils which would have the level of permeability desired and minimal interaction with the wastes. Such a material was found at Mare Island, California; it is a sediment of high silica content from the Sacramento River. The coefficients of permeability of the admixed materials are presented in Table V.

TABLE IV. LINER MATERIALS FOR HAZARDOUS WASTES.

Soil and Admix Materials	Thickness in inches
Asphalt emulsion on nonwoven fabric	0.3
Compacted native fine-grain soil (from Mare Island)	12.0
Hydraulic asphalt concrete	2.5
Modified bentonite and sand	5.0
Soil cement with seal	4.5
Polymeric Membranes:	Thickness in mils
Butyl rubber reinforced	34
Chlorinated polyethylene (CPE)	32
Chlorosulfonated polyethylene (Hypalon) - reinforced	34
Elasticized polyolefin (3110)	25
Ethylene propylene rubber (EPDM)	50
Polychloroprene (neoprene) reinforced	32
Polyester (experimental)	7
Polyvinyl chloride (PVC)	30

TABLE V. PROPERTIES OF ADMIX MATERIALS

	Permeability cm/sec	Remarks
Emulsified asphalt on nonwoven fabric	$< 10^{-8}$	
Hydraulic asphalt concrete	$< 10^{-8}$	Densely compacted
Mare Island soil	$-10^{-8}-10^{-7}$	Fine-grain plastic soil
Modified bentonite and sand (1 to 4, by weight)	2×10^{-7}	Clay swells to form tight barrier
Soil cement	5×10^{-8}	Mixed in place and compacted

The polymeric membranes were selected to represent examples of different polymers. The thicknesses were selected to be as close to the same thickness as possible and yet used practically. Both reinforced and nonreinforced films are included. The butyl rubber, ethylene propylene rubber, and polychloroprene are all vulcanized and require vulcanizable cements for seaming. The remaining membranes are based upon non-vulcanizable polymers which can be seamed by heat, solvents or solvent cements. The experimental heat sealable polyester film was included because of its good resistance to oily wastes.

Selection of Hazardous Wastes

Six classes of hazardous wastes were selected for this test. These are:

- Acidic sludge
- Alkaline sludge
- Cyclic hydrocarbon sludge
- Lead waste from gasoline tanks
- Oil refinery tank bottom waste
- Pesticide sludge

Twelve specific wastes were obtained and a preliminary characterization was made of each. Eleven of these wastes meet the classification and are being included in exposure tests.

The individual wastes and limited data on each are given in Table VI. Both of the tank bottom wastes are satisfactory for the test; however, neither was received in adequate quantity to place in the required number of cells and a third tank bottom waste was collected; it is not satisfactory and a fourth is now being collected.

The wastes were received in 55-gallon drums; several have been found to be inhomogeneous with phase separations taking place. In order to place uniform wastes in the exposure cells, drums of each waste are being blended before loading into the individual cells.

Preliminary Results of Exposing Liners to Caustic Wastes

In order to determine which liners could be used in the experiment to confine the particular wastes that had been collected, exploratory exposure tests were run. Also included in the testing were all of the raw materials which would be used in fabricating the exposure cells and sealing the liners in the cells, i.e. the epoxy coating and the various caulks and sealants. The results of these exposure tests which were run for approximately three months are presented in TablesVII and VIII.

It is quite apparent that some of the liners will not resist some of these wastes, i.e., the modified bentonite liners allow the strong bases and strong acids to seep

TABLE VI. PRELIMINARY CHARACTERIZATION OF WASTES.

CLASS OF WASTE	IDENTIFICATION OF SPECIFIC WASTE	pH	SOLIDS, % TOTAL	VOLATILE	REMARKS
Strong Acid	"HFL"	4.8	2.48	0.29	
	"HNO$_3$, HF, HOAC"	1.5	0.77	0.12	
Strong Base	"Slopwater"	12.0	22.43	5.09	
	"Spent Caustic"	11.3	22.07	1.61	
Tank Bottom	"Weed Oil"	7.5	1.81	1.00	30/60 highly aromatic oil/water.
	"Tergol Clay"	-	71.8	ca 39	Oil and clay.
Lead	"Low lead gas washing"	7.2	1.52	0.53	34 ppm lead.
	"Gasoline Washwater"	7.9	0.32	0.17	11 ppm lead.
	"Mohawk leaded"	7.9	0.73	0.60	5 ppm lead
Saturated and Unsaturated oil		-	ca 36	ca 31	
Pesticide	"Weed Killer"	2.7	0.78	0.46	

Note: Underlined wastes are included in the exposure testing at the base of the cells.

TABLE VII

EFFECT OF IMMERSING LINER MATERIALS IN HAZARDOUS WASTES

Unit: %increase in area of portion of strip immersed

Waste No.		Strong Acid		Strong Base		Tank Bottom		Lead Wastes			
		HFL	HNO_3	Slop Water	Spent Caustic	"Weed Oil"	Tergol Clay	Lo Pb Washing	Gasoline Wash Water	Sat & Unsat Oil	Pesticide Weed Killer
		(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
Membrane Liner	No.										
Polyvinyl chloride (PVC)	10	CC	NVC	HDS	NVC	NVC	-17 HDS	NVC	NVC	-10 HDS	NVC
	11	NVC	NVC	HDS	NVC	NVC	-12 MDS	NVC	NVC	-5 HDS	NVC
	17	NVC	NVC	HDS	NVC	+11	-10 HDS	NVC	NVC	-6 HDS	NVC
	40	NVC	NVC	HDS	NVC	+24	SHD	NVC	NVC	SHD	NVC
reinforced with nylon	49	-	-	-	-	+3	-	-	-	-	-
	59 *	NVC	NVC	HDS	NVC	+26	-6	NVC	NVC	SHD	NVC
	67	NVC	NVC	HDS	NVC	+5	-6 SHD	NVC	NVC	SHD	NVC
reinforced with nylon	71	NVC	[a]	HDS	NVC	CC	-8 HDS	NVC	NVC	-6 HDS	NVC
[a]0.10 in swell each direction, curled, and delaminated.											
Chlorosulfonated Polyethylene (Hypalon) nylon reinforced	6[a]	NVC	NVC	NVC	NVC	R	NVC	NVC	NVC	40	NVC
cured and reinforced	50	-	-	-	-	6	-	-	-	-	-
	55	NVC	NVC	NVC	NVC	-	NVC	NVC	NVC	36	-
Chlorinated polyethylene (CPE)	12[a]	NVC	NVC	NVC	NVC	R	6	NVC	NVC	11	NVC
	38	NVC	NVC	NVC	NVC	R-92	NVC	NVC	NVC	16	NVC
nylon reinforced	39	NVC	NVC	NVC	NVC	R	NVC	NVC	NVC	9	NVC
polyester reinforced	48	-	-	-	-	R[a]	-	-	-	-	NVC
polyester reinforced	73	NVC	NVC	NVC	NVC	-	NVC	BLS	NVC	2-CC	-
[a] Complete loss of tear strength											
Ethylene propylene rubber (EPDM)	8	NVC	NVC	NVC	NVC	75	24	NVC	NVC	77	-
	20[a]	NVC	NVC	NVC	NVC	90	60	NVC	NVC	70	NVC
Polychloroprene (neoprene)	9	CC	SCR	CC	NVC	111	77	NVC	NVC	42	-
	37	NVC	NVC	NVC	NVC	67	NVC	NVC	NVC	21	NVC
nylon reinforced	42	NVC	R	NVC	NVC	REV	NVC	NVC	NVC	5	NVC
	43	-	-	-	-	10	13	-	-	48	NVC
polyester reinforced	47	-	-	-	-	6	-	-	-	-	-
nylon reinforced	56	NVC	NVC	SHD	NVC	100	3	NVC	NVC	10	NVC
reinforced with polyester	74	NVC	NVC	[a]	NVC	NVC	NVC	NVC	NVC	NVC	-
[a]Neoprene ok but reinforcing fabric (polyester) dissolved.											
Butyl Rubber	22	NVC	NVC	NVC	NVC	68	64	NVC	NVC	69	NVC
	24	NVC	NVC	NVC	NVC	91	59	NVC	NVC	89	-
	44	-	-		-	76	13	-	-	94	-
nylon reinforced	57*	NVC	NVC	NVC	NVC	67	20	NVC	NVC	40	NVC

TABLE VII(continued)

Page 2 of 2

EFFECT OF IMMERSING LINER MATERIALS IN HAZARDOUS WASTES

Unit: % increase in area of portion of strip immersed

Waste No. Membrane Liner		No.	Strong Acid		Strong Base		Tank Bottom			Lead Wastes			
			HFL	HNO_3	Slop Water	Spent Caustic	"Wood Oil"	Tergol Clay		Lo Pb Washing	Gasoline Wash Water	Sat & Unsat Oil	Pesticide Weed Killer
			(1)	(2)	(3)	(4)	(5)	(6)		(7)	(8)	(9)	(10)
Elasticized polyolefin (3110)		36	NVC	NVC	NVC	NVC	49	17		NVC	NVC	32	NVC
		41	NVC	NVC	NVC	NVC	42	18		NVC	NVC	24	NVC *
Thermoplastic polyester		69	NVC	NVC	a	NVC	12	NVC		NVC	NVC	NVC	NVC
		75	NVC	NVC	a	NVC	18	NVC		NVC	NVC	9	NVC
Polyurethanes	polyester reinforced	45	-	-	-	-	30	-		-	-	-	-
	polyester reinforced	46	-	-	-	-	44	-	-	-	-	-	-
	reinforced	51	-	-	-	-	2	-	-	-	-	-	-
	nylon reinforced	70	CC	NVC	CC	NVC	33	NVC	-	CC	NVC	14	NVC
	polyester reinforced	72	CC	NVC	CC	NVC	28	NVC	-	NVC	NVC	5	-
Misc. liner materials -	Coal Tar Pitch + PVC	32	NVC	NVC	HDS	NVC	17	NVC	-	NVC	NVC	NVC	NVC
	Emulsified Asphalt on Petromat	38	NVC	SCR/BLS	NVC	NVC	R	R	-	NVC	NVC	R	BLS
Sealing Materials -	Butyl caulk	63	NVC	NVC	NVC	NVC	R	-		NVC	NVC	-	-
	Polyurethane caulk	64	-	R	SFT 1&2	NVC	SFT 1&2	-		NVC	BLS	-	-
	Polysulfide caulk	66	NVC	SFT 1&2	SCR	NVC	NVC	NVC		NVC	NVC	NVC	-
	Teflon sponge rod	68	NVC	rev NVC	NVC	NVC	ABS	ABS		NVC	NVC	ABS	-
	Neoprene sponge	3	NVC	SCR	SHD	NVC	38	SHD	-	SHD	SHD	SHD	SHD

[a] Black rubs off, indicating possible dissolving

NOTES:

* Materials incorporated in cells - underlined.
- Material not tested in the waste noted

Waste No. 1.Hydrofluoric acid
2.Hydrofluoric, acetic and nitric acids
3.Slopwater
4.Spent caustic
5.Wood oil (highly aromatic) 30%;
water 70% (Tank bottom waste)
6.Tergol-clay
7.Low lead gas washings
8.Gasoline wash water
9.Oil (saturated and unsaturated)
10.Pesticide, a weed killer

R - Removed specimen from waste because of excessive swelling or disintegration
NVC - No visible change
SCR - Surface cracking and hardening
HDS - Hardened and shrank
SHD - Slightly hardened
DIS - Dissolved or disintegrated
BLS - Blistering of surface
SFT-1 - Softened above waste
SFT-2 - Softened in waste
SS - Slightly swollen
DEL - Delaminated
CC - Color change
REV - Reverted

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TABLE VIII

EFFECTS OF PLACING WASTES ABOVE TEST SPECIMENS OF ADMIX MATERIALS

Time to first passage of wastes or fraction of waste through material, in days

	Strong Acid		Strong Base		Tank Bottom		Lead Wastes			
	HFL	HNO_3	Slop Water	Spent Caustic	"Wood Oil"	Tergol Clay	Lo Pb Washing	Gasoline Wash Water	Sat & Unsat. Oil	Pesticide Weed Killer
Waste No.[a]	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
pH	4.8	1.5	12	11.3			7.2			
Treated Bentonite-Sand Mixtures										
A -	17d	3d	2d	3d	[illegible]	>47d	>47d	>47d	14d	-
B -	>44d	3d	2d	3d	>47d	>47d	>47d	>47d	>47d	-
Native Soil (Mare Island)	-	>19d	>19d	11[b]	-	-	-	-	-	-
Soil-Cement containing Rice Hull Ash		>19d Bubbling on Surface	>19d NVC	2d[c]	-	-	-	-	-	-
Soil-Cement, Portland	>19d	>19d Surface Softer	>19d NVC	NVC						

[a] See notes on Table VII.

[b] Some dampening of bottom; neutral to litmus.

[c] Fluid passing through is basic.

NVC - no visible change to surface of specimen in 19 days.

through in a relatively short time. Also, almost all of the membrane liners tend to swell in the oily wastes. Such combinations are not being tested as liners in the bases of the cells in the long exposure tests. In the shorter tests, a variety of these materials can be tested by immersion in the various wastes and their properties as affected by exposure can be measured.

These exposure tests have been initiated and will require at least a year before results are available. Shorter term immersion tests will also be run and the results will be available at an earlier date.

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LINERS FOR DISPOSAL SITES TO RETARD MIGRATION OF POLLUTANTS

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ABSTRACT

The potential hazard of polluting constituents from solid waste deposited on land is influenced by the rate they migrate through the soil and/or geologic material to underground water sources and links into the food chain. The rate is controlled by the nature of (a) the solution carrying the pollution constituent, (b) the soil and geologic material through which the constituents move, and (c) the constituent itself. The most prominent properties of the above three habitats which influence migration rate were identified. The measurable soil parameters which most affect attenuation of the selected trace elements (As, Cd, Cr, Cu, Hg, Ni, Pb, Se, V, and Zn) are: clay content, lime, hydrous oxides of Fe, and surface area per unit weight of material. The individual trace elements migrated at different rates through soils. The presence or absence of organic constituents in the influent is a factor in Hg attenuation. The following liner materials are suggested for study on a pilot-plant basis: (a) agricultural limestone, (b) hydrous oxides of Fe (ferrous sulfate mine waste), (c) lime-sulfur oxide (stack-gas waste), (d) certain organic wastes, and (e) soil sealants (independent of the U.S. EPA grant). Preliminary research on limestone and Fe hydrous-oxide liners indicates these materials have a marked retarding influence on the migration rate of many trace elements.

INTRODUCTION

Wastes from which polluting constituents originate, in large part, are deposited either directly on land or end up on land, indirectly, from air and water transport systems. The pollution hazard is intensified greatly if the constituents tend to migrate through the soil and/or geologic debris to underground sources of drinking and irrigation water (Weddle and Garland, 1974). Such wastes, whether municipal, agricultural, or industrial also may pollute through the food chain as a result of adsorption by food and field crops from contaminated soil and water sources.

Although sanitary landfill is one of the approved methods of solid waste disposal, rainwater may permeate the waste, accumulate, and solubilize potentially hazardous constituents. Some of these constituents (including heavy metals) may undergo a series of reactions possibly reprecipitating and resolubilizing several times as they migrate through the landfill and underlying earth materials before finally reaching an underground water source (Miller, et al., 1974). The rate of migration into underground water sources determines the level of potential pollution hazard. The rate of migration varies from those constituents that migrate almost uninhibited to those that may be almost wholly immobilized. This rate is controlled by the nature of the three main components of the wastes habitat; namely, (a) the solution carrying the pollution constituent, (b) the porous medium through which the constituent is being transported, (i.e., the soil or geologic material) and (c) the constituent itself.

Under the usual condition of land disposal, the above waste habitats which influence migration rate receive no particular attention for favorable alteration. Yet, alteration of the pollutants' in situ habitat can decelerate migration. Modern land disposal management dictates that those factors influencing attenuation of pollutants, whether centered in the soil, in the leaching solution, or in the constituent itself, be identified and put to practical work to help control migration.

The mass sampling surveys of garbage dumps, landfills, and indeed a wide variety of disposal sites throughout the U.S. reveal a great variability in the concentration of pollutants in the waters surrounding and below sites (Weddle and Garland, 1974). To a certain extent this situation may be expected, since disposal sites often are located in coarse textured materials, along river bottoms, abandoned gravel and sand pits, rock quarries, and in gaping aggregate-removal sites of the building trades. Basins of such porous media are virtual sieves which retain only the large particles and permit soluble substances to pass through (Garland and Mosher, 1974). Other basins which have been located in finer textured material have been filled with little knowledge developed concerning the physical characteristics of soil and geologic media (i.e., stratifications of texture, structure, density, hydraulic conductivity, cracks, etc.) surrounding the disposal site. Because of the great variability associated with disposal sites as well as solid waste disposal material, and the difficulty of accurately characterizing the heterogenic physical nature of the walls, floor, and surrounding earth materials, it is mandatory that (a) solid waste deposits be located in soil and/or geologic material most favorable for retaining potential pollutants generated by the waste, and (b) something be done to the site pit to insure retention maximization. Pollution control of wastes should not be left to the chances of nature. Studied location selection and site management are necessary. The development of inexpensive liners from waste material is one method to help insure retention of hazardous constituents deposited on land. For this discussion, liners may be described as thin layers of porous material through which liquid must pass. They assume the position of controllable variables because disposal excavations, typified by landfill sites, may be lined easily to various thicknesses of these materials and packed to densities to achieve a favorable flux. In this way, leachates and other wastewaters from disposals must pass through a control barrier before entering the natural soil and geological material.

One of the main requirements of most landfills is that they leak. Leachates collecting from natural precipitation, as well as that applied, must escape. Another requirement is the retention of pollutants within narrow limits of the sides and floor of the landfills. The soils and geologic material associated with landfill sites, vary greatly ranging from those that provide no effective attenuation to those that are somewhat retentive. All sites require modification if migration of pollutants is to be retarded because all natural materials permit migration of at least some polluting constituents found in waste leachates. Liners provide the mechanisms necessary to retain, at least to some extent, the undesirable migration of pollutants. This is a far greater task than completely sealing the site boundaries, although the latter may be necessary at some sites.

To develop a practical site-liner program it was necessary to identify specific factors or properties of each of the three components of the pollutant habitat which influence rate of migration. The most prominent of these factors are described by Fuller and Korte (1976), and Korte et al. (1976a). A more recent complete coverage of this subject appears in a U.S. EPA contract report by Fuller (1976). Some of the on-going research at the University of Arizona relating to attenuation of trace elements in soils also will be reported by Korte et al. (1976b), Alesii et al. (1976), and Skopp et al. (1976), at this symposium. Among the outstanding soil parameters which influence the attenuation of the 12 selected trace elements are the content of clay, lime, and hydrous oxides.

The main thrust of this research report will be to suggest possible low-cost waste material liners for disposal sites to retard migration of trace elements, including some heavy metals. In the chemical literature "heavy metals" generally refers to those metals which have densities >5.0. In this report "trace elements" will refer to As, Be, Cd, Cr, Cu, Fe, Hg, Ni, Pb, Se, V, and Zn.

MATERIALS AND METHODS

SOILS

Eleven soils representing 7 major orders were collected throughout the U.S. at depths below the organic laden top-soil. Although the soils were not collected entirely in the C horizons and parent material profile position common to the location of many landfills, the selection provides an opportunity for a clearer evaluation between soil characteristics and attenuation, the main purpose of this research. Furthermore, disturbed soil material, taken from landfill excavations for covering, enveloping, "cell" encasing, etc., usually is required and accepted as a management practice. Other land deposits such as the containment from air and water pollution involves soil contact. Thus, if others characterize a soil-like material from a greater depth, for example, they can take note of the characteristics of the soil material used in this study and select the one most similar to their location. Knowledge of the behavior of dominant and readily measurable soil parameters in attenuation provides a basis for establishing control-prediction.

Some physical characteristics of the soils collected are shown in Table 1. The clay contents range from 3 to 61%. The clay minerals of the >2μ separate of the 11 soils varied widely from largely montmorillonite-type in Anthony s.l. and Chalmers si.c.l. to largely Kaolinite-type in Davidson and Molokai clays and Wagram l.s. The pH values range from 4.2 for the Ultisol, Wagram l.s. to 7.8 for the alkaline Aridisols, Anthony s.l. and Mohave$_{Ca}$ c.l. Other characteristics are described in detail in earlier publications by Fuller and Korte (1976).

MUNICIPAL LANDFILL LEACHATE

The natural leachate used as a vehicle for carrying the individual "spiked" potential pollutants (Al, As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Se, V, and Zn) came from a municipal solid waste landfill (Korte, Niebla, and Fuller, 1976). The trace element was "spiked" at concentrations of 1000 ppm for Al, Cu, and Pb, and 100 ppm for all other elements although lower ranges of 25 to 85 ppm also were used for those elements which form anions. Such concentrations were established for convenience of identifying attenuation effect of the liners since the individual elements differ widely in their rate of migration through the liner barriers.

LINER MATERIALS

Liner materials considered for study were ground limestone ($CaCO_3$), sand treated with hydrated $FeSO_4$, and soil treated with hydrated $FeSO_4$. The ground limestone is a commercial product from Cedar Bluff, KY, commonly used for agricultural soil applications. Particle size analysis of this 98% pure $CaCO_3$ appears in Table 2. Two particle size distributions of the limestone were used, namely (a) the original material as it is sold, and (b) the same material sieved to pass a 0.5 mm screen.

The treated sand and soil liners were prepared by spraying the sand and soil with aqueous $FeSO_4$ to attain a final $FeSO_4 \cdot 7H_2O$ concentration of 1% by weight.

PROCEDURE

A series of "batch" studies were conducted preliminary to the more definitive "column" studies. The batch technique is simpler and less expensive so was used initially to determine (a) maximum adsorption interaction between selected trace elements and limestone, (b) appropriate concentration levels of spiked element which would provide measurable data in the column studies, and (c) the effect of limestone particle size when used as a liner material.

The details of the soil column procedure have been described by Korte, et al. (1976) and by Fuller (1976). In brief, 10-cm lengths of 5 cm PVC pipe were filled with soil to form a vertical soil column. The procedure and equipment used in the

TABLE 1. CHARACTERISTICS OF THE SOILS

Soil	Order	pH	CEC	EC	Surface Area	Free Iron Oxides	Total Mn	Sand	Silt	Clay	Texture Class	Predominant Clay Minerals*
			meq/ 100g	µmhos /cm	m^2	%	ppm	%	%	%		
Wagram (N.Carolina)	Ultisol	4.2	2	225	8	0.6	50	88	8	4	loamy sand	Kaolinite, Chlorite
Ava (Illinois)	Alfisol	4.5	19	157	62	4	360	10	60	31	silty clay loam	Vermiculite Kaolinite
Kalkaska (Michigan)	Spodosol	4.7	10	237	9	1.8	80	91	4	5	sand	Chlorite, Kaolinite
Davidson (N.Carolina)	Ultisol	6.2	9	169	51	17	4100	19	20	61	clay	Kaolinite
Molokai (Hawaii)	Oxisol	6.2	14	1262	67	23	7400	23	25	52	clay	Kaolinite Gibbsite
Chalmers (Indiana)	Mollisol	6.6	26	288	126	3.1	330	7	58	35	silty clay loam	Montmorillonite, Vermiculite
Nicholson (Kentucky)	Alfisol	6.7	37	176	121	5.6	950	3	47	49	silty clay	Vermiculite
Fanno (Arizona)	Alfisol	7.0	33	392	122	3.7	280	35	19	46	clay	Montmorillonite, Mica
Mohave (Arizona)	Aridisol	7.3	10	615	38	1.7	825	52	37	11	sandy loam	Mica, Kaolinite
Mohave$_{Ca}$ (Arizona)	Aridisol	7.8	12	510	128	2.5	770	32	28	40	clay loam	Mica, Montmorillonite
Anthony (Arizona)	Entisol	7.8	6	328	20	1.8	275	71	14	15	sandy loam	Montmorillonite Mica

*Listed in order of importance

TABLE 2. A COMPARISON OF PARTICLE SIZE DISTRIBUTION OF TWO COMMERCIAL AGRICULTURAL LIMESTONE MATERIALS FROM TWO KENTUCKY SOURCES

Sieve Size Classes		USDA Texture Classes	Sieve Size and Source of Limestones	
			Lexington	Cedar Bluff
			- - - - - -%	- - - - - -
-2.5 to -2.0	-5.66	gravel	0.9	0
-2.0 to -1.5	5.66 to 2.80		17.3	5.1
-1.5 to -1.0	2.80 to 2.00		13.2	4.4
-1.0 to -0.5	2.00 to 1.40	very coarse sand	15.2	6.8
-0.5 to 0	1.40 to 1.00		11.4	7.8
0 to 0.5	1.00 to 0.71	coarse sand	10.2	8.3
0.5 to 1.0	0.71 to 0.50		7.5	9.4
1.0 to 1.5	0.50 to 0.355	medium sand	8.3	12.5
1.5 to 2.0	0.355 to 0.250		6.0	10.2
2.0 to 2.5	0.250 to 0.180	fine sand	3.0	6.7
2.5 to 3.0	0.180 to 0.125		2.4	6.3
3.0 to 2.5	0.125 to 0.090	very fine sand	1.5	4.8
3.5 to 4.0	0.090 to 0.063		1.0	6.0
	0.060 to 0.050		0.8	1.9
	< 0.050	silt + clay	1.2	9.9

quartz sand column study to evaluate the attenuating effect of liner material independent of soil differed from the soil column studies only in that acid washed quartz sand was used instead of soil. The top 2 cm of the column consisted of the liner material to be evaluated. The solution carrying the spiked trace element being studied was in all cases natural municipal landfill leachate. The solution was displaced through the column until the effluent concentration of the spiked trace element was equal to the concentration in the influent.

Potential liner-soil medium combinations are:

1. Limestone layered over quartz sand,
2. Limestone layered over soil,
3. $FeSO_4$ treated sand layered over quartz sand,
4. $FeSO_4$ treated sand layered over soil,
5. $FeSO_4$ treated soil layered over quartz sand, and
6. $FeSO_4$ treated soil layered over soil.

RESULTS AND DISCUSSION

This presentation is represented by a limited amount of data since the liner phase of the grant program has been underway only a few months. Agricultural limestone and the hydrous oxides of iron received the most attention.

LIMESTONE

There was essentially no difference in influence on adsorption of trace element attributable to particle size of limestone, so data from only the sieved limestone (<0.5 mm) are given here. The degree of adsorption varied among trace elements and among different contact time intervals (Figure 1). Lead, Cu, and Al, for example,

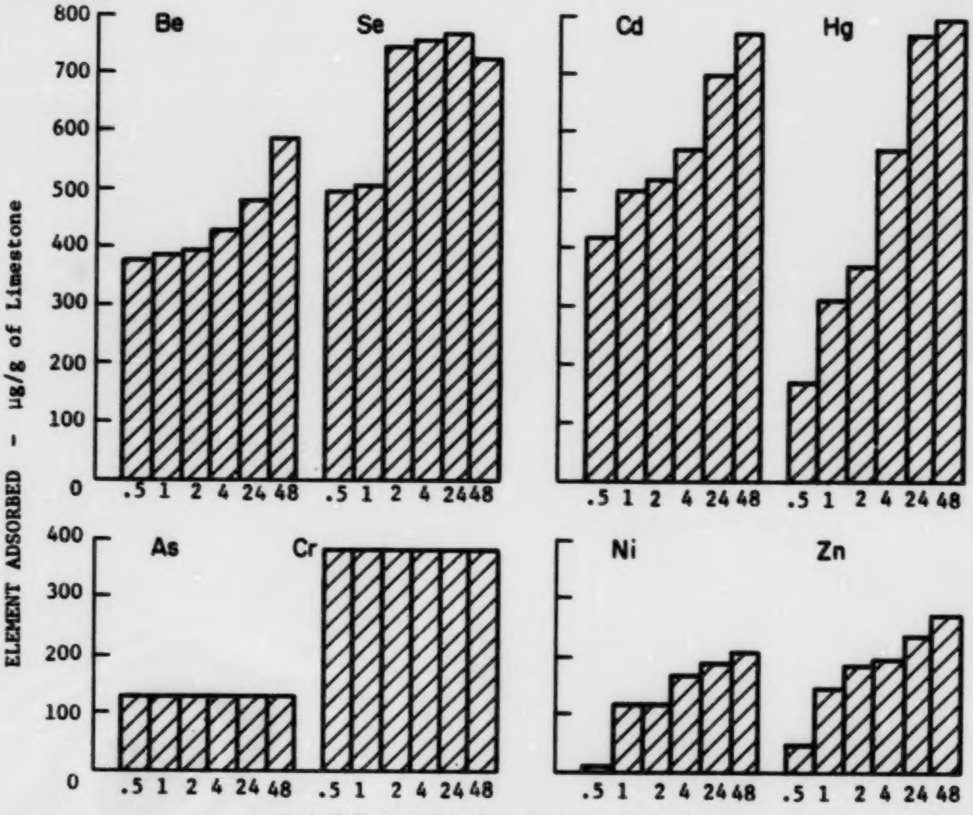

Figure 1. The adsorption of As, Be, Cd, Cr, Hg, Ni, Se, and Zn, from municipal landfill leachate, by Kentucky agricultural limestone as influenced by time of contact.

were adsorbed much more entensively than other elements (Table 3 and Figure 2)

TABLE 3. THE ADSORPTION OF TRACE ELEMENTS FROM MUNICIPAL LANDFILL LEACHATE BY KENTUCKY AGRICULTURAL LIMESTONE AS AFFECTED BY CONTACT TIME

Spiked Element	Contact Time	Supernatant pH	Supernatant Ca	Supernatant Spiked Element	Element Sorbed by Limestone
	hours		ppm	ppm	µg/g
Ni	0.5	6.1	270	115	0
	1	6.2	200	97	120
	2	6.2	200	98	120
	4	6.3	250	93	170
	24	6.3	390	91	190
	48	6.4	330	89	210
	Tank	5.0	150	110	-
Zn	0.5	6.0	270	109	50
	1	6.1	300	95	150
	2	6.2	325	91	190
	4	6.2	350	90	200
	24	6.4	390	86	240
	48	6.4	440	82	280
	Tank	5.0	130	110	-
Cr	0.5	6.1	390	0	260
	1	6.2	335	0	260
	2	6.2	370	0	260
	4	6.3	380	0	260
	24	6.4	390	0	260
	48	6.3	450	0	260
	Tank	3.1	150	26	-
Cr	0.5	6.5	560	46	380
	1	6.4	549	46	380
	2	6.4	548	45	387
	4	6.6	548	43	435
	24	6.6	520	48	375
	48	6.6	520	48	380
	Tank	2.9	108	85	-
Cd	0.5	5.7	190	39	470
	1	5.7	190	36	500
	2	5.8	190	35	520
	4	5.9	190	29	570
	24	6.0	240	17	700
	48	6.0	300	9	770
	Tank	5.0	130	86	-

TABLE 3 (Continued)

Spiked Element	Contact Time	Supernatant			Element Sorbed by Limestone
		pH	Ca	Spiked Element	
	hours		ppm	ppm	µg/g
As	0.5	6.3	270	37	58
	1	6.3	270	35	73
	2	6.4	270	33	95
	4	6.3	325	32	99
	24	6.4	370	35	73
	48	6.5	370	36	61
	Tank	5.1	130	43	-
As	0.5	6.2	346	90	133
	1	6.2	303	90	133
	2	6.3	333	90	133
	4	6.4	371	90	133
	24	6.5	415	90	133
	48	6.6	443	90	133
	Tank	5.1	136	103	-
Be	0.5	5.6	480	64	380
	1	5.7	480	64	383
	2	5.6	510	63	393
	4	5.7	500	60	427
	24	5.7	500	54	482
	48	5.8	570	35	590
	Tank	4.0	130	103	-
Hg	0.5	6.3	270	83	167
	1	6.4	320	69	311
	2	6.4	330	63	369
	4	6.4	370	43	570
	24	6.5	380	23	769
	48	6.4	420	21	794
	Tank	5.1	130	100	-
Se	0.5	6.2	260	8	267
	1	6.3	260	5	295
	2	6.4	285	4	310
	4	6.3	300	3	319
	24	6.5	325	4	305
	48	6.5	370	5	298
	Tank	5.1	130	35	-
Se	0.5	6.3	314	45	510
	1	6.2	328	45	510
	2	6.2	300	22	745
	4	6.4	300	23	760
	24	6.5	377	23	770
	48	6.5	391	23	725
	Tank	4.9	189	96	-

TABLE 3 (Continued)

		Supernatant			
Spiked Element	Contact Time	pH	Ca	Spiked Element	Element Sorbed by Limestone
	hours		ppm	ppm	µg/g
V	0.5	6.3	400	89	210
	1	6.5	427	77	335
	2	6.5	501	76	345
	4	6.5	500	75	350
	24	6.5	500	76	330
	48	6.6	500	75	325
	Tank	4.6	115	110	-
Cu	0.5	5.3	120	500	300
	1	5.4	130	395	2500
	2	5.9	240	30	5100
	4	6.1	280	4	5360
	24	6.3	320	4	5360
	48	6.3	540	5	5360
	Tank	4.5	150	540	-
Cu	0.5	5.4	327	875	1575
	1	5.4	366	832	2000
	2	6.0	944	19	10,025
	4	6.4	963	8	10,125
	24	6.4	1001	8	10,124
	48	6.4	1025	6	10,126
	Tank	4.5	130	1032	-
Cu	0.5	5.1	332	1186	1985
	1	5.1	404	1169	2153
	2	5.9	1098	56	13,286
	4	6.3	1175	18	13,665
	24	6.3	1329	12	13,725
	48	6.3	1146	7	13,772
	Tank	4.5	130	1385	-
Al	0.5	5.9	2000	0	8500
	1	5.9	2160	0	8500
	2	5.9	2160	0	8500
	4	6.0	2160	0	8500
	24	5.9	2200	0	8500
	48	6.0	2200	0	8500
	Tank	3.7	130	850	-
Pb	0.5	4.7	160	645	2200
	1	4.9	180	590	2700
	2	4.5	160	560	3000
	4	4.9	180	433	4325
	24	5.8	300	13	8520
	48	5.9	380	2	8630
	Tank	3.1	130	865	-

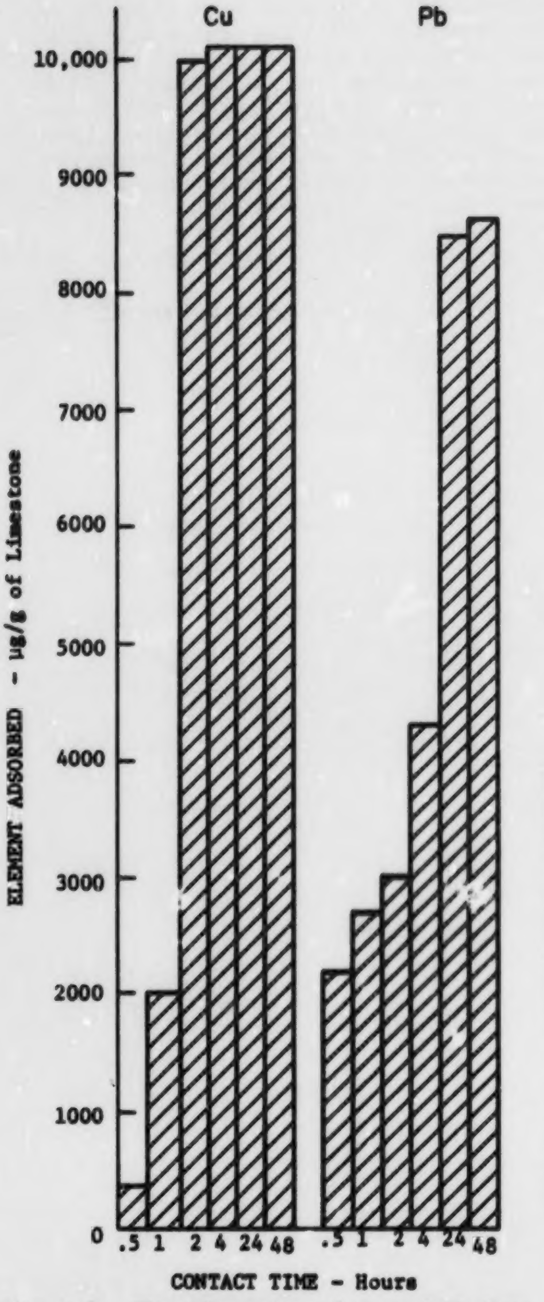

Figure 2. The adsorption of Cu and Pb from municipal landfill leachate by Kentucky agricultural limestone as influenced by time of contact.

and adsorption was enhanced by greater contact time. Also, in general, the longer contact time between the spiked effluent and limestone increased the concentration of Ca in the supernatant and raised the pH level (Table 3). In certain cases such as with Al, Cu, Cr, and Pb, adsorption by the limestone did not reach a maximum because the element was depleted from the leachate within the time limit established. Adsorption comparisons among these elements must therefore be interpreted as less than maximum, particularly during the longer contact time intervals. The attempt to overcome this by increasing the concentration of element "spiked" (As, Cu, Cr, Pb, Cu) did not achieve the goal. The limestone only succeeded in adsorbing more of the element (Table 3).

Commercial grind limestone used in the sand and soil column studies in which one column was overlaid by 1 cm of limestone and the other by washed quartz sand, reduced the migration rate of Cd through Wagram l.s. (Figure 3). A similar experi-

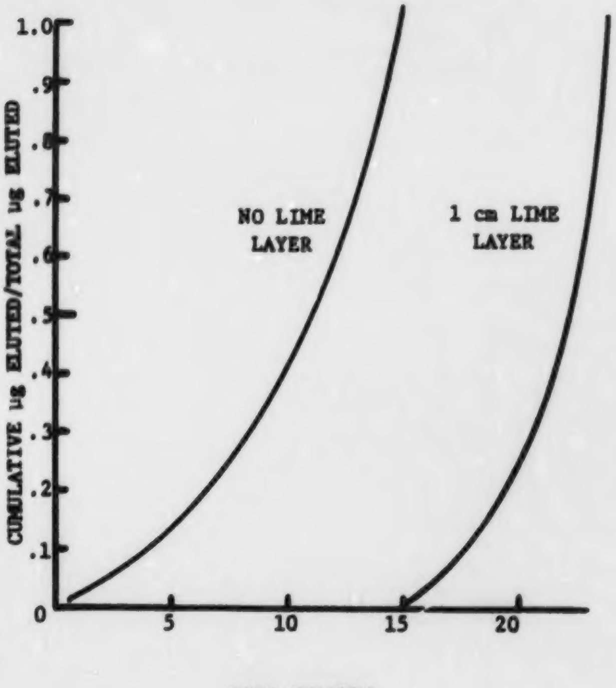

Figure 3. Effect of ground agricultural limestone liner on movement of Cd through Wagram l.s.

ment was undertaken to determine the migration rate of Ni with similar results (Figure 4). Those elements which form anions, namely, As, Cr, Se, and V appear to be the least subject to retention by limestone liners associated with soil (Figure 4).

The results from the "batch" studies appear to be in disagreement with those of the "column" studies. The former makes it appear that the anion-forming elements may be retained by the limestone as well if not better than some strict cations since their adsorption from the leachate follows this pattern. Compare Se, As, and Cr with Ni and Zn in Figure 1, for example. Limestone layered in soil columns, however, had no measurable attenuating influence on Cr above that of either Wagram l.s. or Anthony s.l. alone (Figure 4). Cadmium and Ni moved through soil material much less

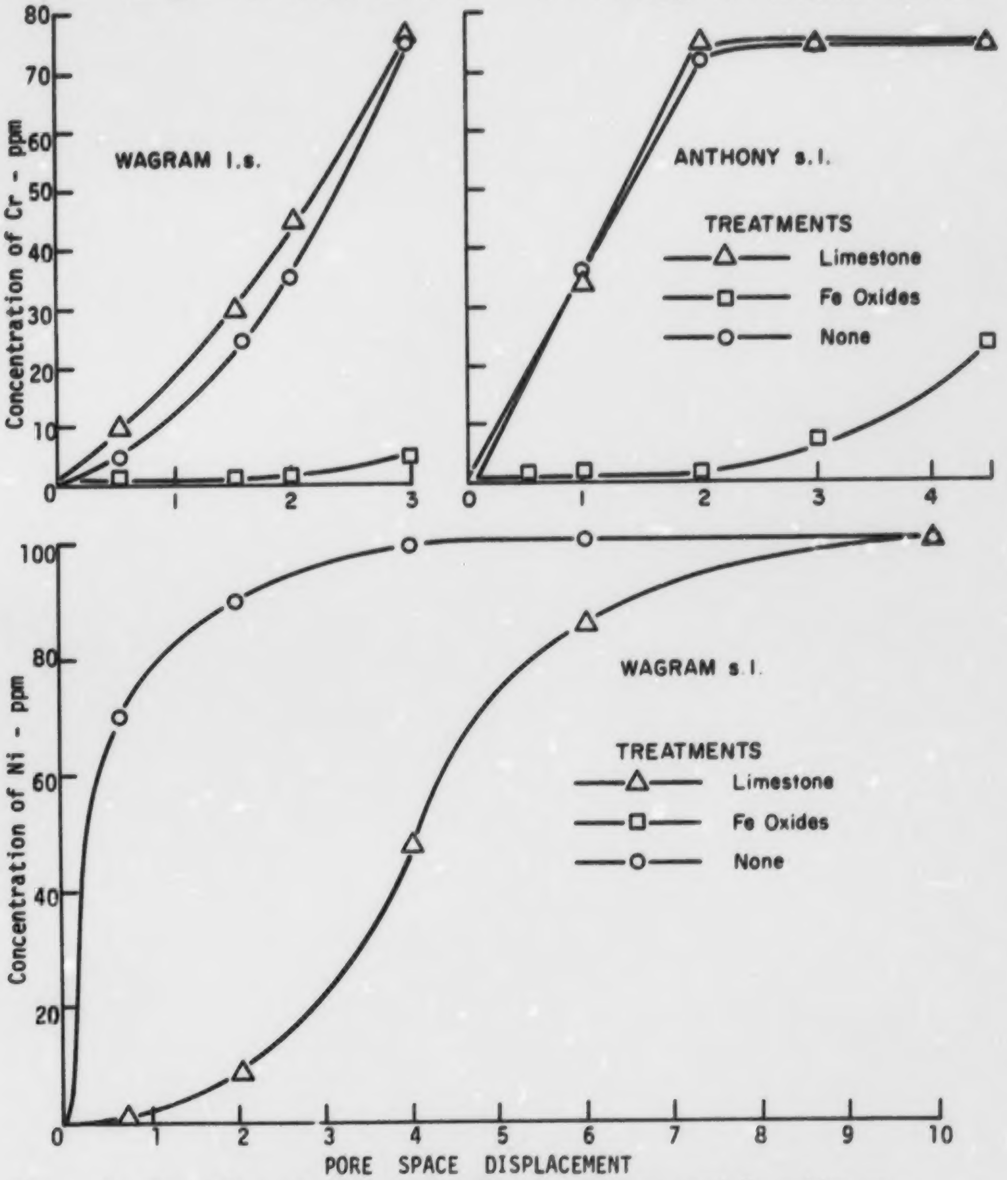

Figure 4. The effect of ground agricultural limestone and Fe oxides on element retention.

rapidly in the presence of a thin limestone layer than in its absence. Again compare Figures 3 and 4. The data imply that elements adsorbed by limestone may or may not lose their capacity to migrate when exposed to the leaching action of the solution. In other words, different elements may be held by the limestone at different levels of tenacity and some are displaced more readily than others. For example, the anion-forming elements appear to be held less tightly to the limestone than most of the strict cations. The capacity of limestone to adsorb an element from solutions, as in the batch technique, does not necessarily imply an extent or degree of retention of that element against migration.

Another factor is the capacity of the soil alone to react differently to possible resulting constituents formed as the different elements pass through limestone. The soil beneath the liner may become an added factor in migration which may be supporting, undoing, or indifferent to the effects of the limestone depending on the specific element involved. An example in which the limestone layer appears merely to offset the retention effect of soil is shown in Figure 3 illustrating the migration of Cd through a Wagram l.s. column. The soil in this case appears to be independant of the limestone effects.

Although the "batch" technique does not appear to reflect trace element migration characteristics through a limestone layer as well as the "column" technique (i.e., limestone layer over soil in a column), the procedure still offers promise as a rapid screening aid since many of the 12 trace elements were taken out of solution similarly by both techniques.

When limestone liners are used on acid soils, unnecessary mixing should be avoided since the limestone will react with the soil in neutralizing the acidity. Thus its potential as a barrier for attenuation will be consumed or inactivated to a degree directly proportional to the extent it disappears in soil neutralization.

LIME-SULFUR OXIDES (STACK-GAS WASTES)

Lime-sulfur oxide slurries from air pollution control of stack gases from coal burning appear to have residual potential for controlling pollution because of their content of unspent lime and accumulation of sulfur oxides. However, undesirable characteristics may accompany the use of these slurries. These are the presence of (a) potential hazardous heavy metals, (b) certain slowly degradable hydro-carbons, and (c) possible carcenogenic tars and resins. The management of the slurries also offers a problem in the transport and actual physical lining. In contrast, limestone quarries have long been developed for agricultural soil liming purposes and therefore offer much less of a transportation problem of distance and quality of active attenuating agent.

FERROUS-SULFATE (MINE WASTE)

Ferrous sulfate accumulates as a waste product of copper mines. When applied to soil the iron sulfates rapidly change to insoluble hydrous oxide forms. The iron oxides have the capacity to coat soil particles readily forming very thin layers which are highly active in attenuation processes. The effectiveness of ferrous sulfate as an attenuator of pollutants has been studied in column studies.

Quartz sand and soil columns were prepared by sprinkling the corresponding materials with ferrous sulfate mine waste at a calculated rate of 1% Fe_2O_3 by weight of the upper 2 cm in the column. The effect of hydrous oxides of Fe on attenuation of Cr in Wagram l.s. (pH 4.2) and Anthony s.l. (pH 7.8) are compared with limestone in Figure 3. Chromium migration is clearly retarded by the presence of the hydrous oxides of Fe. Significant correlations have been reported (Korte et al., 1976; and Fuller, 1976) to occur between percentage trace element retained by soil and "free" iron oxide content. Davidson and Molokai clay soils have the highest content of extractable "free" iron oxides and also unusual high capacity to retain trace elements, which is over and above clay effect. Another point of interest is the highly significant correlation found between iron oxide and total soil Mn. The importance of Mn or hydrous oxides of Mn is not fully known although it is suggested to be less significant in attenuation than iron oxides. The practical research reported here agrees with the pure-system chemical research of Jenne

(1968) and Gadde and Laitinen (1974).

ORGANIC WASTES (e.g., NUTSHELLS)

The abundance of nut shells that are available for disposal near sanitary landfills could be used as liners to assist in retaining heavy metals and other trace elements. They have great capacity for adsorbing metallic ions. Under the anaerobic conditions of many disposal sites the rate of decomposition of nutshells is particularly slow, probably in the order of many years. Data on possible "leak" rate for trace elements are not available.

Because of the organic matter content of many wastes disposed of on land and in soils, the question of chelation as a factor in downward migration of pollutants through soils and geologic material understandably is raised. This is not a new question but one which has been researched by soil scientists involved with plant nutrition and radioactive fall-out pollution control. For example, after many years of intensively studying movement (or lack of movement) of inorganic phosphates in soils, P was found by Fuller and his colleagues (see Hannapel et al., 1964a, 1964b) to move downward through soil primarily in organic chelates. The same movement of ^{90}Sr and ^{45}Ca through soil was found to be enhanced by the association with organic matter and chelates (Fuller et al., 1966, 1968; and L'Annunziata and Fuller, 1968). Thus, organic chelation as a mechanism influencing attenuation is established. Such mechanisms likely function in long-term migration of polluting constituents through soils not only with landfill leachates and organic waste waters, but also in long-term land application of municipal sewage sludges. Indeed, much research is needed before quantitative data can be generated in sufficient amount to aid in prediction of organic initiated contaminant movement through soils and geologic materials.

SOIL SEALANT (SALT)

Some land disposal sites should be made completely impervious to leaking. Despite the existance of a low water table overladen with soil materials possessing naturally favorable attenuation properties, if the water from the site reaches the capillary fringes of the sub-surface water, it will contain some soluble constituents which could contribute to quality deterioration. Many examples of this punctuate the history of irrigated agriculture in arid lands (Fuller, 1975; Muller, et al., 1973; and Richards (1954). Fortunately, where soils are deep, and underground aquafers are deep and flowing, accumulations of salts and other pollutants may not take place sufficiently to threaten water quality. This is made evident by many years of irrigated agriculture located over deep alluvium in the western states without appreciable alteration of underground water quality.

Artificial lakes have been successfully sealed in the southwestern desert areas using natural clay soil material[1]. The procedure involves lining the lake or site boundaries with clay saturated to 25% of its cation-holding-capacity with sodium. The clay liner is compacted moist but not wet at about 40% of normal field-holding capacity. The aim is to approach maximum possible density of compaction.

Prior to establishing artificial lake or disposal sites, soil cores are taken to the site depth and analyzed for clay content at 1-foot intervals. The clay laters are plotted and stockpiled during excavation for lining. If clay does not occur in the excavation it must be brought in from another area.

Liners for complete sealing seldom measure less than 30 cm of clayey soil and often approach a thickness of 60 cm if the percentage clay is low. Both cation-exchange-capacity and particle size distribution (mechanical analysis for texture) must be known to make liner recommendations. The dominant clay mineral composition helps considerably for establishment of confidence limits for successful sealing.

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[1] Private communication of first author.

CREDITS

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LEACHABILITY AND PHYSICAL PROPERTIES OF CHEMICALLY STABILIZED HAZARDOUS WASTES

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ABSTRACT

The disposal of hazardous industrial waste sludges by landfilling has the potential for an undesireable environmental impact due to leachate production and concommitant pollutant migration. Chemical fixation of sludges is a viable treatment alternative which may reduce this undesireable environmental impact. The U. S. Army Engineer Waterways Experiment Station (WES), through an interagency agreement with the U. S. Environmental Protection Agency, is currently evaluating fixation technology to assess its role in sludge disposal operations. The current program is divided into three phases involving the characterization of the raw sludges, laboratory leaching and physical testing of raw and fixed sludges, and pilot scale leach testing of raw and fixed sludges. The results presented within this paper will be confined to one of the five hazardous industrial waste sludges, namely the electroplating sludge. Results of the physical testing to be presented include bulk density, void ratio, porosity, specific gravity, and permeability. These results have demonstrated that physical properties of the fixed products are processor dependent and vary in quality. The results of the leaching tests show that all fixed materials are leaching pollutants to some degree. Comparison between the leaching data for the raw and fixed sludges demonstrates that leaching properties are dependent on the pollutant analyzed. Based on the results presented in this paper, fixation appears to be a viable alternative for reducing adverse environmental impact of sludge disposal.

INTRODUCTION

The disposal of wastes to land may result in an adverse environmental impact, particularly if these wastes contain hazardous materials. Interaction of wastes and physical, chemical, and biological mechanisms may permit the environmental transport of hazardous pollutants at unacceptable rates. To avoid this adverse environmental impact, a treatment of these wastes may be required prior to disposal.

Waste material which may be classified as being potentially hazardous include sludges or residues arising from industrial wastewater treatment processes. These treatment processes are specifically designed to remove toxic pollutants from water, and concentrate them in a solid residue or sludge. Land disposal of such residues may result in release of these pollutants to the surrounding ecosystem. The most prevalent pathway for this migration is through an aqueous medium. To retard the movement of pollutants from residues, several concepts may be applied during or prior to disposal. Creation of a barrier between the environment and waste material by lining disposal sites is one option. Investigation of disposal site characteristics to assess its ability to prevent pollutant migration constitutes another option. Alternately, the waste may be treated by a process designed to convert it into a product in which pollutant mobility is retarded. This latter concept may be termed chemical fixation if it takes place by chemically altering the waste material.

Chemical fixation is a process which generally produces a material in which the waste is contained within an inert matrix. Additionally, the fixation process may chemically alter the state of the pollutants within the waste material to reduce their mobility. To successfully apply chemical fixation in the treatment of industrial sludges or residues, the process must be evaluated to insure that it will work in the fashion for which it is designed. Since sludges are generally very heterogeneous mixtures of materials, evaluation must of necessity be on restricted categories of sludges. Evaluation should include assessment of physical and chemical properties with respect to stability.

The most direct test of chemical stability is a leaching test. The leaching test must be executed in such a fashion as to realistically simulate the potential environmental migration of pollutants from the fixed material. Physical properties of the fixed material are important to the extent that they affect leaching properties; therefore, the results of physical and chemical testing must be integrated to assess the merits of fixation.

The U. S. Army Engineer Waterways Experiment Station, through an interagency agreement with the U. S. Environmental Protection Agency, has embarked upon a program to evaluate the chemical fixation of sludges. Within the current program ten sludges are being tested in combination with seven fixation processes. This paper will present preliminary data for one of the industrial waste sludges.

METHODS

Materials

The sludge under study originated from an electroplating industry as a product of wastewater treatment. The sludge is currently disposed by ponding and samples were obtained from the present disposal site. This material contains approximately 39 percent solids and the major pollutants are the metals. The principle metals of interest in the sludge are chromium, nickel, copper, zinc, and cadmium. Calcium is also present in large amounts as a result of treatment processes utilized. This raw sludge will be designated as R-200 for the remainder of this paper. Samples of the sludge were fixed by three commercially available fixation processes and will be designated A-200, B-200, and C-200 respectively.

Physical Testing

Physical tests performed on specimens of raw and fixed sludge included determination of bulk density, void ratio, porosity, specific gravity, and permeability. With the exception of permeability, all tests were performed in accordance with American Society for Testing and Materials (ASTM) procedures (1). Permeabilities were determined by use of a falling head permeameter for the raw sludges and by use of a triaxial testing machine for the fixed sludges.

Chemical Analysis

Leach Testing

Leach testing was performed on the raw and fixed sludges. The procedures and experimental conditions for the leach testing have been documented elsewhere (2,3). All leach testing was conducted in triplicate, and blank columns were used for controls. Two leaching solutions of different pH, 4.7 and 7.5, were employed.

Elutriate Test

The elutriate test as modified (4) was utilized as a rapid leach test and involved the following procedures:

(a) Prepare a 1:4 (V/V or W/V) mixture of material and water at pH 4.7

(b) Mix on a wrist action shaker for one hour

(c) Centrifuge at 2500 rpm for 30 minutes

(d) Filter centrifugate using a 0.45μ filter

(e) Analyze filtrate for desired constituents.

Total Analysis of Specimens

A total analysis of raw and fixed sludge specimens was determined by digesting a sample in a mixture of hydrofluoric and nitric acid. The resultant digest was analyzed for the desired metals.

RESULTS

Physical Properties

The results of the physical properties tests are presented in Table 1.

TABLE 1

PHYSICAL PROPERTIES OF RAW AND FIXED SLUDGES

SAMPLE ID	BULK DENSITY (LB/CF)	VOID RATIO	POROSITY (%)	SPECIFIC GRAVITY	PERMEABILITY (CM/SEC)
R - 200	63.5	3.015	75.2	3.27	1.3×10^{-6}
A - 200	100.4	1.200	54.7	2.65	4.1×10^{-7}
B - 200	67.1	3.162	76.0	2.94	1.2×10^{-5}
C - 200	73.4	1.251	55.6	1.81	1.1×10^{-6}

In general, the bulk density is increased for fixed sludges, and the void ratio, porosity, specific gravity, and permeability are reduced. For samples B-200 and C-200, the permeabilities are increased after fixation. In the case of B-200 this may be explained by noting that process B results in a fixed material physically resembling a soil.

Chemical Properties

Results of the total digest for the raw sludges and fixed products are presented in Table 2. Note that in most cases concentration of metals are reduced by fixation. The only exception to this is in the case of calcium for sample A-200; this is probably the result of calcium being present in the fixation additive. Decreasing concentrations of metals for the fixed sludges is advantageous since it is tantamount to a mass dilution effect.

TABLE 2

RESULTS OF TOTAL DIGESTS

SAMPLE ID	METAL CONCENTRATION (%)					
	Ca	Cd	Cr	Cu	Ni	Zn
R - 200	3.06	0.069	5.78	3.65	0.23	0.68
A - 200	2.63	0.041	4.65	3.02	0.19	0.55
B - 200	4.63	0.025	1.83	0.96	0.09	0.20
C - 200	-	0.010	1.42	0.68	0.05	0.14

The results of the leaching tests are presented by the type of pollutant considered. The mean results for the control columns are presented for all leaching results. This method has the dual advantage of establishing background concentrations to assess the true value of leaching and also to present an overall summary for the quality of the experimental design. The leaching results presented in this paper apply only to the acidic leaching solution. A comparison between leaching solutions will be made subsequently in this paper.

Specific conductivity, which is proportional to dissolved solids, is presented in Figure 1. The raw sludge is

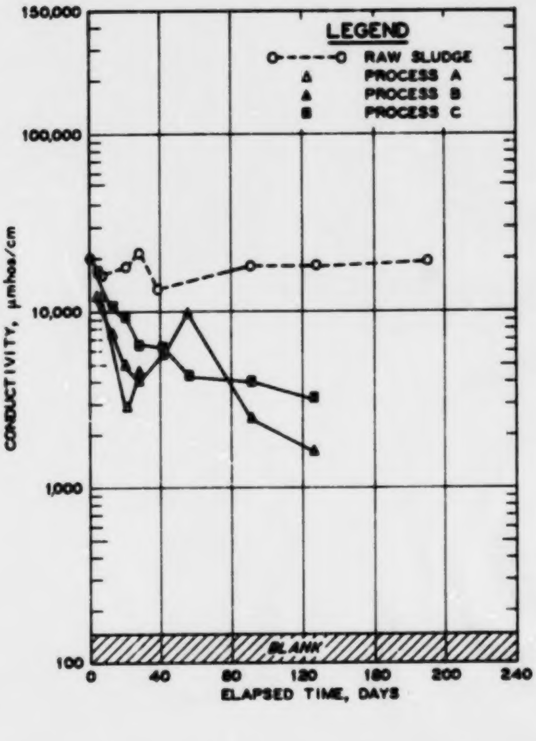

Figure 1. Leaching Results, Conductivity.

characterized by a relatively constant leach rate, while the fixed materials demonstrate a reducing leach rate as a function of time. The background level is low, demonstrating a good blank and leaching of pollutants from all specimens.

The leaching curves for sulfate and chloride are presented in Figures 2 and 3, respectively. These anions represent pollutants which are ubiquitously present in most sludges. These leaching curves demonstrate a constant rate for the raw sludges and decreasing rates for the fixed materials. In all cases the fixed sludges are leaching at lower rates than the raw sludges. For chloride, the leachates from the fixed columns converge to the blank level quickly, indicating that chloride is rapidly eluted from these specimens. In the case of sulfates the leach rates for the fixed specimens are declining but the leachates continue to contain significant concentrations of sulfates.

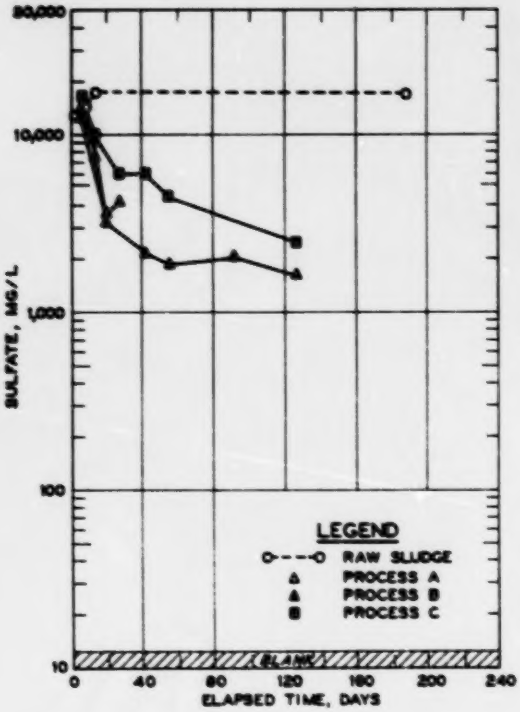

Figure 2. Leaching Results, Sulfate

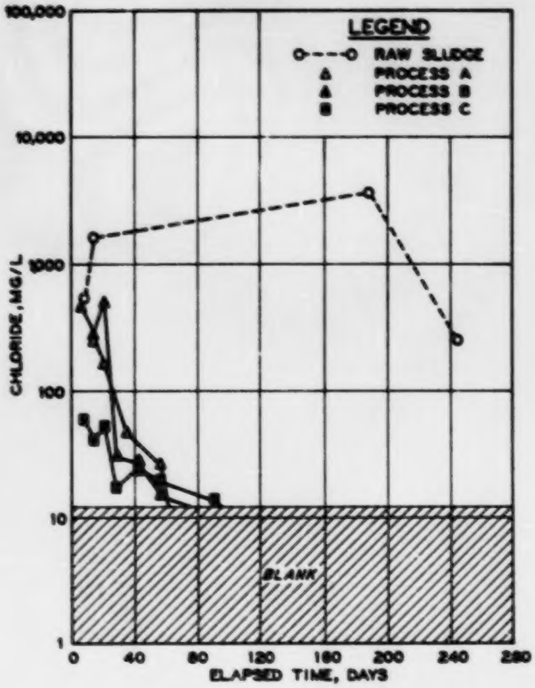

Figure 3. Leaching Results, Chloride

The leaching curves for the metals; calcium, cadmium, chromium, copper, nickel and zinc are presented in Figures 4 through 9, respectively. The leaching curves of calcium demonstrate that the raw and fixed sludges are leaching equally. There appears to be no decline for calcium within the time frame of the data plotted. Calcium is present in large concentrations, Table 2, for all specimens tested. It is presumably being leached at a solubility limited rate and the columns will probably continue to exhibit equivalent leach rates until the available calcium becomes limited. For cadmium, nickel, and zinc, Figures 5, 8, and 9, the leaching properties for the specimens appear to be similar. In all cases one of the fixed specimens demonstrates a significantly higher leach rate for these metals than the raw sludge. In the case of cadmium and zinc the raw sludge and the remainder of the fixed specimens demonstrate rapidly decreasing leachate concentrations. For nickel the leachate from the raw sludge appears to be relatively constant. The leaching curves for chromium and copper, Figures 6 and 7, appear to be similar with the leachate concentrations for the fixed sludges being equal to or greater than the raw sludges. This fact is particularly noticeable in the case of chromium. For the raw sludges the leach rates appear to be relatively stable while those of the fixed sludges are decreasing as a function of time.

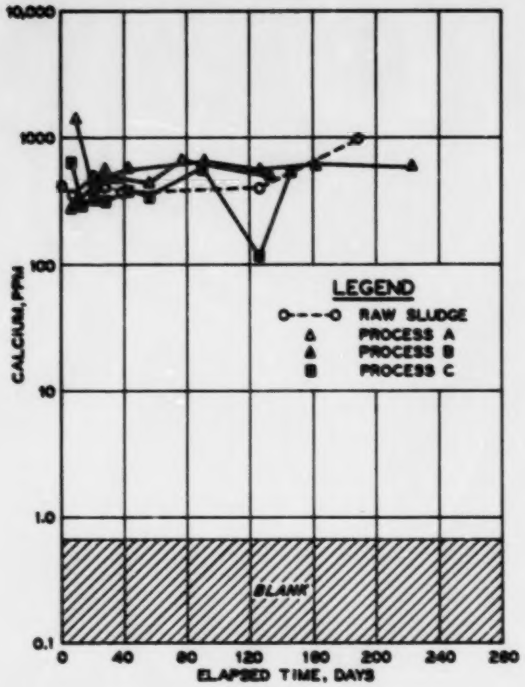

Figure 4. Leaching Results, Calcium.

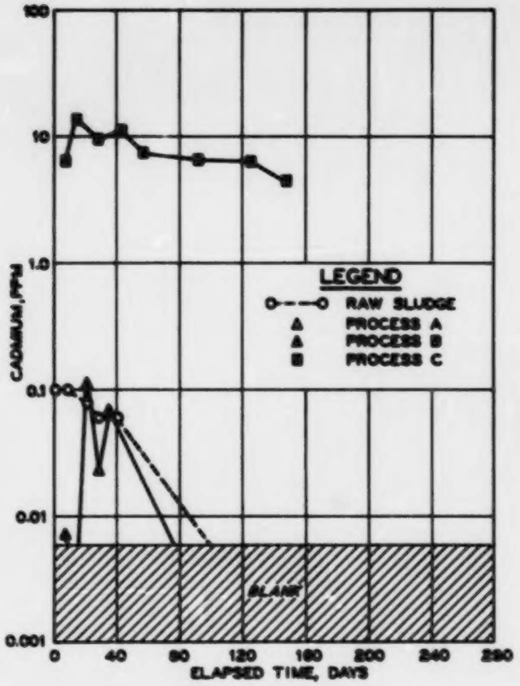

Figure 5. Leaching Results, Cadmium.

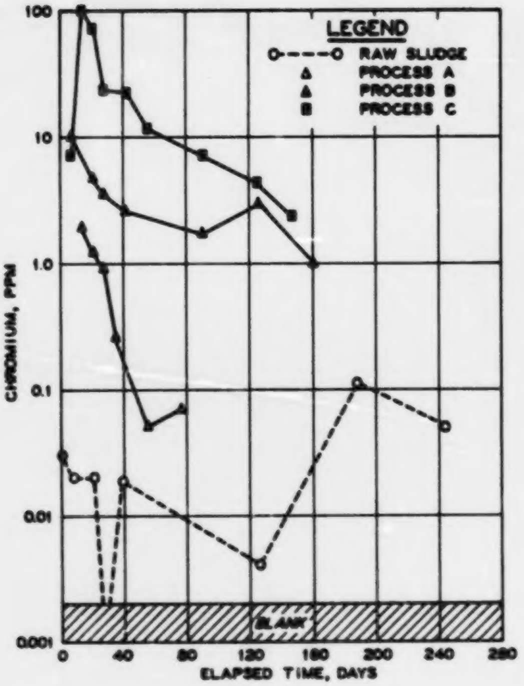

Figure 6. Leaching Results, Chromium

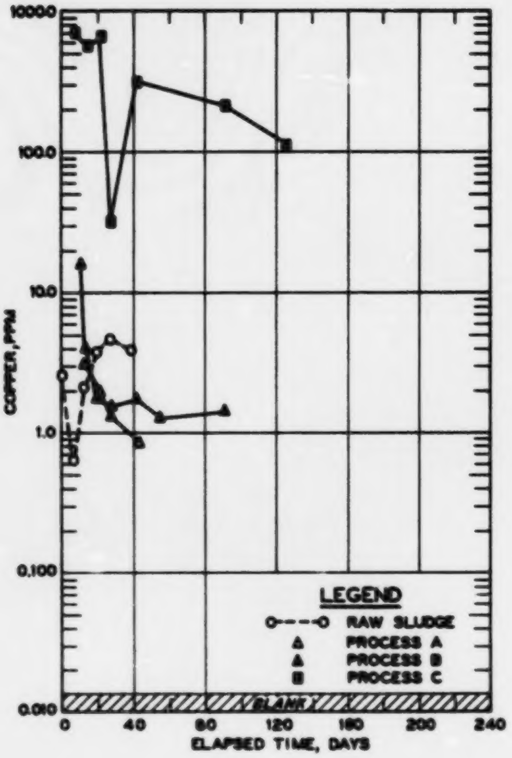

Figure 7. Leaching Results, Copper

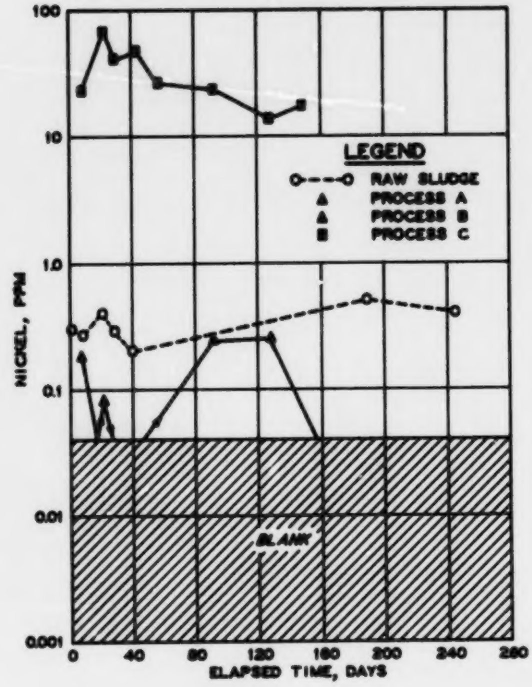

Figure 8. Leaching Results, Nickel.

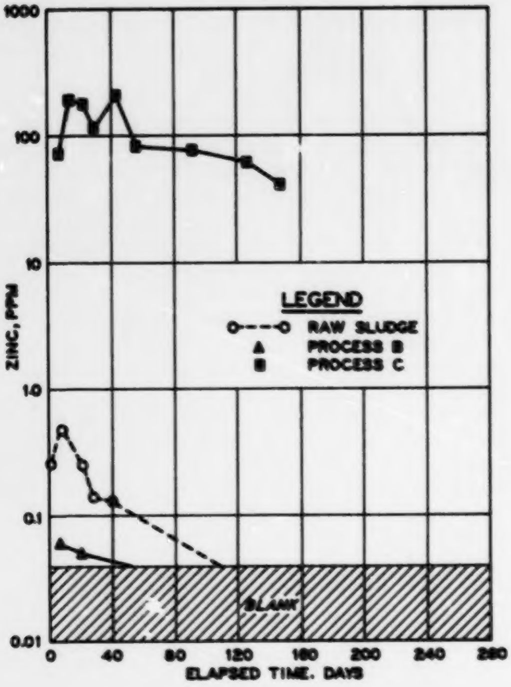

Figure 9. Leaching Results, Zinc.

DISCUSSION OF RESULTS

The leaching of pollutants from the specimens tested in this experiment appears to be a function of the physical and chemical mechanisms operative on these specimens. The effect of any biological mechanism on pollutant mobility is probably insignificant due to the low organic content of these materials. It is apparent from the data presented that the physical and chemical mechanisms are interactive.

The results of fixation are generally manifested by a consolidation or cementing of the sludges into a definite shape. This fact is confirmed by the decreasing porosity, void ratio, and increasing bulk density of the fixed materials. This apparent alteration of physical geometry changes the principle mechanism for mobility of pollutants between the raw and fixed sludges. For the raw sludges the principle mechanism must be assumed to be solubilization of the pollutants from the sludge solids to the aqueous medium. In the case of the fixed sludges, the migration mechanism is solubilization coupled with diffusion of pollutants to the surface of the fixed materials. It is assumed that the diffusion step is the rate limiting event for this mechanism.

The operation of these mechanisms may in part be confirmed by observing the comparative leach behavior of the raw and fixed specimens. The raw sludge is characterized by stable leach rates for most pollutants indicating a solubilization proportional to the concentrations of pollutants present. Those pollutants demonstrating a decreasing leach rate for the raw sludge would indicate a chemical interaction decreasing the solubilities of these consitituents, or a decrease in pollutant available for elution. The fixed sludges demonstrate a decreased leach rate as compared to the raw sludge, particularly for the more mobile species, chloride and sulfate. This fact would tend to indicate that diffusion, and not solubility, was the rate limiting step, confirming the mechanism proposed previously. Calcium behaves in a similar fashion except that the solubility step has not depleted the available calcium allowing a diffusion mechanism to become dominant. For the remaining metals it must be assumed that similar mechanisms are operative, although for process C it appears that something is stimulating metal mobility. Chromium appears to be operating in a like manner, but the fixation process appears to have increased the solubility of this metal.

An additional factor which must be considered is the effect of permeability on sample leaching. The experimental design for the fixed specimens utilizes a surrounding solid medium which is relatively permeable compared to the fixed specimens, except for the B sample. In this case the operation of a diffusion mechanism is almost guaranteed by the column hydrodynamics. For B-200 this is not as evident since the material occupies the entire cross sectional area of the leaching column; however, this sample did alter the physical configuration of the sludge and the diffusion mechanism may be assumed to be operative in a limited sense.

The comparison of leaching data in terms of concentrations does have the advantage of allowing a ready interpretation of possible environmental impact for the experimental design employed. Interpretation of the leaching data in terms of mass of pollutant mobilized has the advantage of presenting a more quantitative picture of the results. An additional tool which may be employed is to calculate apparent diffusion rates for the specimens tested. These rates may be calculated from the following equation (5):

$$\frac{\Sigma a_n}{A_o} \frac{V}{S} = 2 {\frac{D_e}{\pi}}^{1/2} t^{1/2}$$

Where:

a_n = mass of pollutant leached in n periods

A_o = initial mass of pollutant present in the specimen

V = specimen volume

S = specimen surface area (effective)

D_e = effective diffusion rate

t = leachate renewal time

The results of these calculations are presented in Table 3 for copper during four leaching periods. Figure 10 contains the plots of the leaching data for copper in the format of the above equation. The plots in Figure 10 demonstrate the following concepts:

(a) Data between fixed replicates appear to be very precise except for the case of process C, and for this process the slopes are comparable.

(b) The data for the raw sludges do not conform well to this plotting format, indicating a lack of a diffusion mechanism.

TABLE 3

SUMMARY OF LEACHING RESULTS, COPPER

TREATMENT	TOTAL MASS LEACHED (mg)	MEAN LEACHATE CONC (mg/ℓ)	EFFECTIVE DE (cm²/DAY)	ELUTRIATE MASS (mg)
RAW	2.5	2.47	1.28×10^{-16}	2.10
A	21.0	2.03	1.25×10^{-9}	0.23
B	91.0	3.65	2.29×10^{-11}	0.94
C	4553.0	485.00	2.70×10^{-6}	152.00

Table 3 also contains the results from the elutriate tests and the mean concentration of copper leached during the noted time frame. It is apparent that little or no comparison is possible between leachate data for the raw and fixed sludges for the parameters utilized. Between the fixed sludges a very good correlation may be obtained for all parameters. The only conflict appears to be for the effective diffusion rates for process A and B.

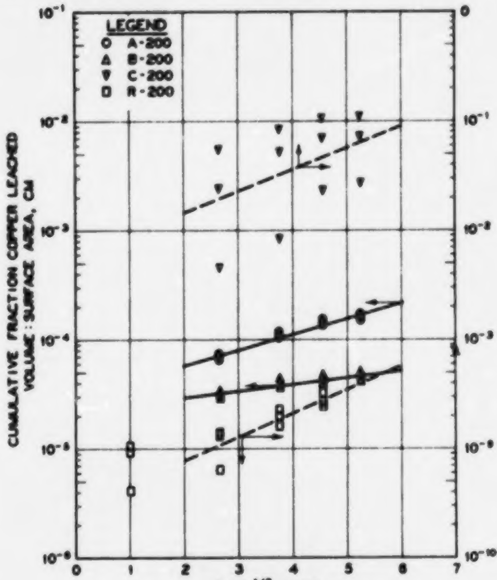

Figure 10. Diffusion Plot, Copper

This may be explained in part by noting that the volume to surface ratio is very influential on the outcome of the diffusion rate calculated. For sample B-200 there is no adequate method for easily determining this ratio and a value was assumed for these calculations; therefore, the value for D_e may be in error. The values for D_e for process A and B fall within acceptable values (5).

The results of the elutriate test for all metals plus pH and conductivity are presented in Table 4. These values correlate well with the results of the leaching data presented earlier. This fact would seem to indicate that the elutriate test or some modification of it may prove to be a reliable indicator procedure for assessing the leaching of raw and fixed sludges.

TABLE 4

RESULTS OF ELUTRIATE TEST

SAMPLE ID	pH	CONDUCTIVITY	MASS OF POLLUTANT ELUTED (mg)					
			Ca	Cd	Cu	Ni	Zn	Cr
R-200	7.2	3.0×10^3	340	0.05	2.10	0.51	0.96	0.09
A-200	6.4	3.0×10^3	336	0.03	0.23	0.05	0.04	0.53
B-200	6.6	4.5×10^3	323	0.06	0.94	0.05	0.04	5.40
C-200	5.1	5.7×10^3	382	1.30	152.00	17.90	40.60	1.60

To obtain an overall assessment of the leaching data from the columns, a procedure known as discriminant analysis was employed (6,7). Discriminant analysis allows the comparison of multivariate populations on a reduced dimensional plane by the construction of a functional relationship between the variables and the reduced space. If the "discriminant" functions are well correlated to the original variable set, then the data may be interpreted graphically. To apply this procedure the leaching variables plotted, (Figures 1-9) plus pH were subjected to discriminant analysis. The data set included the first four leaching periods, the results from both leaching solutions, and all control column results. The results of the discriminant analysis are shown in Figure 11 as a plot of the data sets for the first two discriminant functions (accounting for 85 percent of the data variance).

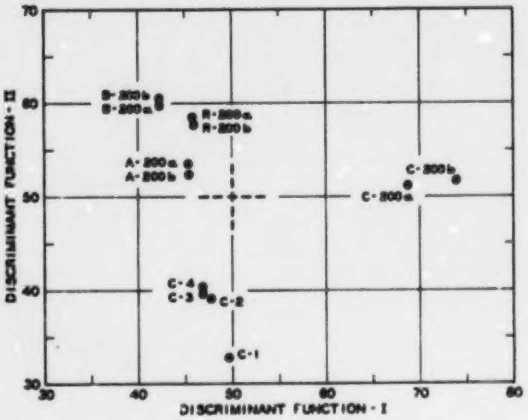

Figure 11. Leaching Results, Discriminant Plot.

An examination of Figure 11 demonstrates that little difference exists for the results in terms of leaching solutions applied. This was somewhat expected from prior knowledge regarding properties of these sludges and was confirmed by this analysis. This result would presumably justify elimination of applied pH from consideration as one of the major variables affecting leachate quality. To gain a greater insight to the meaning of this plot, an examination of the correlation of the discriminant functions with the original variable space is required. The first discriminant function is inversely related to leachate pH and directly related to chromium, nickel, zinc, copper, and cadmium concentrations. The second discriminant function is directly related to conductivity, sulfate, chloride, and calcium. These relationships have meaning of their own merit; the first discriminant function indicating a close, inverse correlation between heavy metals and pH and the second indicating a direct correlation between conductivity and the anions plus calcium. The plots are made relative to a value of 50 for each discriminant function, thus the distance for the centroid of the plot is proportional to the deviation from the grand mean for that sample.

Examining Figure 11, it is observed that the control columns occupy the lower left quadrant indicating a negative (lesser) deviation from the overall leaching data. The fixed samples for process C occupy the middle right quadrant indicating a high leaching of metals, but average leaching rates for the remaining pollutants. The raw sludges and those samples fixed by processes A and B occupy the upper left quadrant indicating comparable leachate quality. In general, the results of this analysis may be confirmed by an examination of the leachate data presented previously; however, this comparison is between those data sets included in the analysis and may tend to bias the results.

A realistic assessment relating to the environmental effects of a fixed sludge must, of necessity, include some consideration of scaling parameters associated with field disposal. This assessment is related to the diffusion mechanism which is presumably operating for fixed materials and the exposed surface area at a disposal site. To make a preliminary evaluation of this concept the data for copper from R-200, A-200, and B-200 during the first four leaching periods and both leaching solutions were examined. For the case of a diffusion mechanism, the leachate quality is a function of the initial mass of pollutant (i.e., copper) present in the specimen.

Figure 12 is a plot of mass of copper leached versus percent copper present in the specimen. A regression analysis of the data demonstrated no dependence between copper present in the sample and the leachate copper mass for the raw sludge. If the previously proposed mechanism is correct, then this should be observed, as it was. Conversely, for the fixed specimens a significant dependence was demonstrated between copper initially present in the specimen and mass leached. This fact tends to confirm the diffusion mechanism previously alluded to in this paper.

To apply these results to a field condition it is necessary to correct the data for the fixed samples in Figure 12

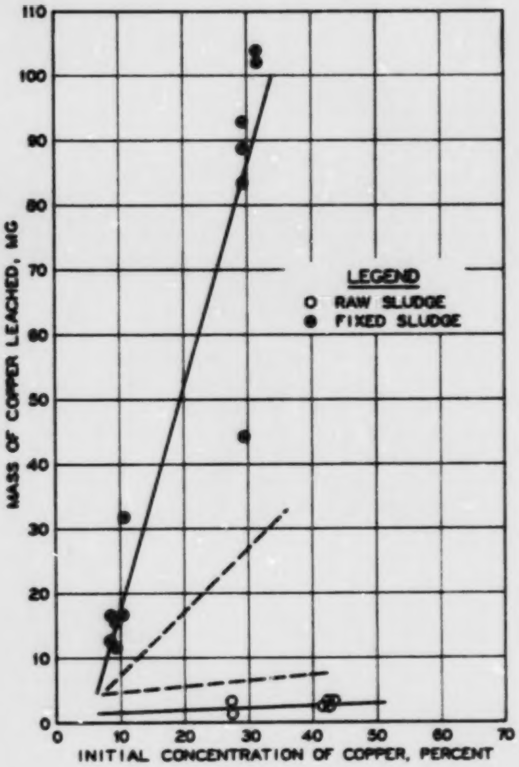

Figure 12. Mass Leaching, Copper.

for the exposed surface area. This is shown in Figure 12 by the dotted lines; the upper divergence reflecting the confidence limits on the surface area assumption for B-200. This data may be applied to the field by making the following assumptions:

(a) The depth of material placed for the raw and fixed sludges is equivalent.

(b) The densities of all materials (raw and fixed) are approximately equal.

(c) The pollutant mass from the raw sludge is a linear function of the surface area exposed at the bottom of the disposal site.

(d) The pollutant mass produced from the fixed materials is a function of the leach rate and exposed sidewall area.

(e) The leachate quality produced from fixed material is proportional to the mass dilution imposed by fixation.

The results of this analysis are presented in Figure 13 as a plot of tons of sludge disposed versus milligrams of copper in the leachate. This figure demonstrates that fixation possesses a definite advantage over raw sludge disposal on the basis of the copper data and the assumptions made.

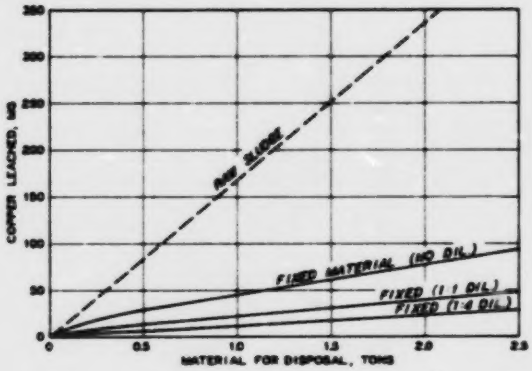

Figure 13. Field Scale Disposal Relationship, Copper.

The effect of mass dilution by fixation additives is also apparent. The curves for the fixed and raw materials appear to be converging at the lower end of the graph. This would in general be the case, where the raw material would serve as an upper bound for mass leached. It should be stressed that these results are based on an analysis of one pollutant, and in general, an evaluation would be required for all environmentally hazardous constituents being produced by the sludge.

CONCLUSIONS

As a result of the data obtained from the study on raw and fixed electroplating waste treatment sludges, the following conclusions may be made:

(a) Chemical fixation of sludges is manifested by physical and chemical alterations of the parent material. As a result of these alterations the mechanisms for leaching and its associated environmental impact are altered.

(b) The effect of the pH of leaching solutions applied to specimens in this study was insignificant in the pH of the leachates. The effect of this variable, within a reasonable range of values, may be considered minimal.

(c) The relation of laboratory data obtained in this study to field disposal conditions is an integral phase of fixation assessment. An evaluation conducted in this paper demonstrated that fixation is a viable alternative for reducing pollutant migration from sludges.

(d) The modified elutriate test appears to offer a satisfactory method for rapid evaluation of the leaching of raw and fixed sludges, although the data are not interchangeable.

It should be stressed that these conclusions reflect a limited analysis of the data obtained from the present study. An individual consideration of all major pollutants is necessary to completely describe the potential environmental impact associated with sludge disposal. Furthermore, the assumptions related to field scale disposal operations must be validated and related to the laboratory tests.

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A POLYMERIC CEMENTING AND ENCAPSULATING PROCESS FOR MANAGING HAZARDOUS WASTE

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ABSTRACT

A process using polymeric materials to cement and encapsulate dry hazardous waste was researched, developed, and evaluated. The process involves cementing particulates of waste into 500 to 1000 pound agglomerates, and then fusing a plastic jacket onto the agglomerate surfaces, thereby encapsulating them. Polybutadiene, as a binder resin, was found to be capable of cementing waste 94 to 96 percent by weight of the agglomerate. The binder exhibits properties that contribute to ready processing of the agglomerates. Encapsulating the waste-binder agglomerates with 1/4-inch jacket of high density polyethylene can be carried out by packing powdered polyethylene about the agglomerate and then fusing the powder in situ. The method was satisfactorily applied to produce laboratory specimens containing, in some cases, high concentrations of highly water soluble heavy metal wastes, e.g., sodium metaarsenate. Test specimens were subjected to leaching solutions for 120 days and mechanical stresses to evaluate the processes' capability to isolate the hazardous waste from selected disposal environments. Results indicate the processes' ability to prevent, or limit to acceptable levels, the release or delocalization of the hazardous waste to the environment under various disposal schemes. This paper discusses the process and provides results of the evaluations.

INTRODUCTION

Under Section 212 of the Resource Recovery Act of 1970, the Environmental Protection Agency became responsible for the preparation of a Report to Congress defining the various aspects of the hazardous waste problem (1,2). The report was based on specific contract efforts designed and programmed to provide the information and insight necessary to the presentation of a complete and accurate picture. One contract identified a number of hazardous materials, their sources and quantities, and the technology utilized for their treatment. Another contract had three concurrent objectives: (1) to refine the listing of hazardous wastes based on further information, (2) to analyze and assess current hazardous waste disposal technology, and (3) to define research and development necessary to provide information or adequate technology (3).

The quantity of industrial and municipal wastes generated in the United States is increasing faster than the population. The diversity of these wastes preclude the utilization of a single method or technology to provide adequate treatment and/or disposal. As a result, a number of methodologies and technologies are in use, or have evolved and are under development (4). In addition, recycling and utilization of wastes are being examined as techniques to limit the quantity of waste which must be provided ultimate disposal. Although this alternative is attractive, only limited success is being claimed. Also, reality must be faced; technologies are not likely to emerge which will detoxify all components of hazardous wastes. There will most likely always be some form of toxic residuals (wastes) which must undergo ultimate disposal.

Of particular concern are those wastes with the potential to harm man and/or the environment. The hazardous wastes may be either in the solid state or mixed with a liquid, most often water, in the form of sludges, slurries or slimes. Almost any branch of modern industry, metallurgical, chemical, ceramic, mineral, food processing, metal treatment, petroleum refining, treatment of municipal sewage, etc., generates some kind of wastes; described varyingly as tailings, scraps, rubble, garbage, refuse, residue, sludge, slime, slurry, mud, etc. These wastes often contain toxic compounds including arsenic, lead, mercury, selenium, beryllium, cadmium, zinc, and chromium. The potential hazard is increasing rapidly due to the greater quantities of concentrated toxic solids and sludges being produced by control policies and equipment designed to limit air and water pollution.

One recommendation of the hazardous waste studies led to the implementation of additional research to more fully investigate "fixation" as a solution to the problem of providing acceptable disposal of hazardous wastes. In July 1973, SHWRD awarded a research contract to TRW, Inc. to expand proof-of-principle and feasibility testing of two processes for passifying toxic waste. One process utilized polymeric materials to form, contain, and isolate toxic solids; while the other process relied upon inorganic materials. The ultimate objective of the research and development was to provide a process capable of localizing and limiting the release to the natural environment of toxic waste materials to levels consistent with control strategies and with both short term and long term protection of the environment. Most important were hazardous wastes that could not be adequately localized by available techniques.

The initial phase of the research program was designed to determine information on three important process characteristics: (1) the technical behavior of the processes; (2) the ability of the processes to passivate (localize) hazardous wastes; and (3) the process economics. Waste simulants were used to ease the handling problems and to insure a known baseline for the process development and evaluation. A number of different organic and inorganic cements and jacketing materials were tried in various proportions. The effectiveness of the processes to isolate the wastes was determined on the basis of results of leach tests using various solutions in which passivated waste blocks were immersed. Preliminary design and economic analysis were also determined for both the organic and inorganic cementation processes.

Results of the first year's work are available and describe results of tests on both the "organic" and the "inorganic" process.* Although promising, the process utilizing inorganic materials was judged as not sufficiently unique in its approach to warrant additional EPA support. Additionally, the process did not appear to be suited to the adequate control of "extremely" hard to manage hazardous waste, such as arsenicals, for which other available processes were judged not adequate. Therefore, SHWRD directed TRW to cease work on the inorganic process and to concentrate their efforts on additional research development, and evaluation of the "organic" (polymeric) process.

Based upon results of the initial studies high performance resins were selected for the waste-binder agglomerization and for the jacketing (encapsulation). The additional studies concentrated on the following: (1) to show general applicability of the selected resins to passify hazardous waste regardless of their chemical compositions, (2) to provide an encapsulation process suitable for large scale operations, (3) to evaluate and demonstrate, if possible, the performance characteristics of the process when subjected to harsh environmental stresses and, (4) to provide initial process designs and economic information.

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The purpose of this paper is to describe the "organic" or polymeric process. Details of process description, process development and evaluation, process applicability, limited economics, and additional information will be presented.

PROCESS DESCRIPTION

The polymeric process used to passify the selected hazardous waste involves the following basic steps (Figure 1):

- dewatering of sludges
- coating the waste particulate with the resin
- evaporating the solvent carrier
- agglomerating the waste particulate--resin
- compacting by thermo-setting to form a waste-binder block, and,
- encapsulating the waste-binder block (jacketing).

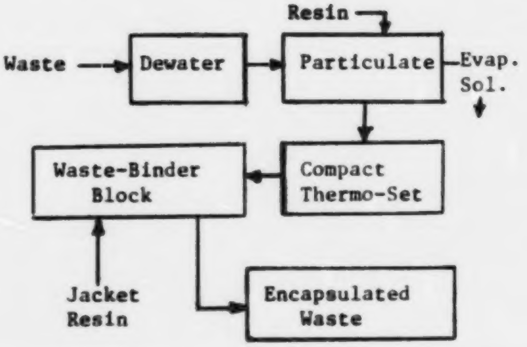

Figure 1. Schematic of the Polymeric Process for Stabilizing Waste

Resins selected for forming the waste-binder agglomerate and the jacket were modified polybutadiene and polyethylene respectively. This selection was based upon results of the earlier study on resin screening and the following criteria:

- High loading ability, i.e., small amounts of resin must be capable of agglomerating and cementing large amounts of waste particulates.

- Chemical stability of the agglomerate waste.

- Ability to readily wet solid waste particulate.

- Easy and rapid formation of resin coated waste agglomerate for a wide variety of waste materials.

- Uniform distribution of resin in the agglomerate.

- High heat distortion temperature (HDT) to allow for wide selection of resin for jacketing; fusion of coating resin to the cemented waste core should not cause any dimensional distortion of the compacted core block.

- Low cost.

- Stability under normal conditions: no special precautions for resin storage.

- Satisfactory fluidity of waste/resin agglomerate particulate for fast and thorough filling of mold for compacting by thermosetting.

- Long "pot life" to allow the processing time to vary widely.

Because of flexibility in their formulation, hydrocarbon resin systems in general are excellent candidates for passifying, by agglomeration and encapsulation, heavy metal compounds. However, certain stereo-configurations of polybutadienes were found to be particularly applicable for forming an agglomerate of waste and binder. Those selected are liquid and polymerize easily because of the high content of unsaturated bonds.

The polybutadiene and polyethylene resins in combination were found to yield high performance, passivated waste products. This assessment could not be applied distinctly to other resin systems; consequently, the polybutadiene-polyethylene resin system appears unique for passifying wastes by agglomeration and encapsulation. Included in the assessment were product processing techniques. Technological barriers to ready reproducible processing of encapsulated wastes are markedly reduced by the physical and chemical character of these resins.

Prior to agglomerating 4 percent w/w polybutadiene resin coated particulated wastes, it was considered important to

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observe the free flowing character of the particulates and their shelf stability. Free flowing particulates facilitate loading of large molds for subsequent thermal fusion of particulates into large agglomerates. The property of shelf stability places essentially no time constraints upon initiating fusion operations. These advantages contribute to ease of making passivated products. The product performance is consequently less sensitive to the mechanics of product fabrication. All resin coated particulates freely flowed and agglomerated readily (Figures 2, 3, 4, and 5).

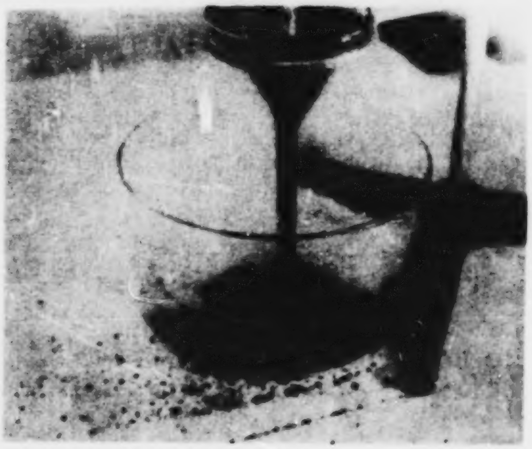

Figure 2. Polybutadiene Coated Residue of Sludge 200

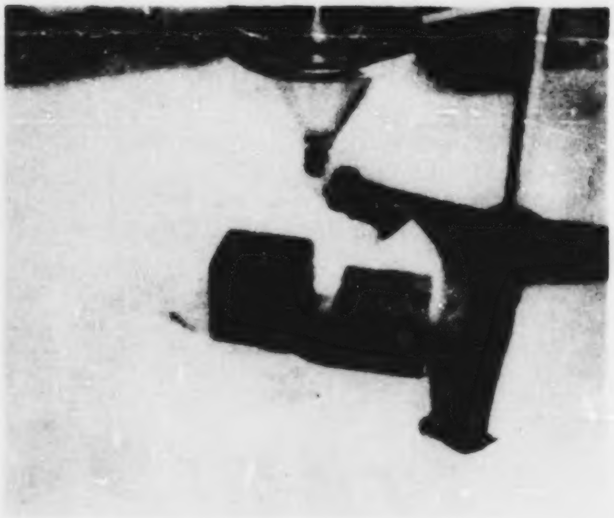

Figure 3. Fused Residue of Sludge 200

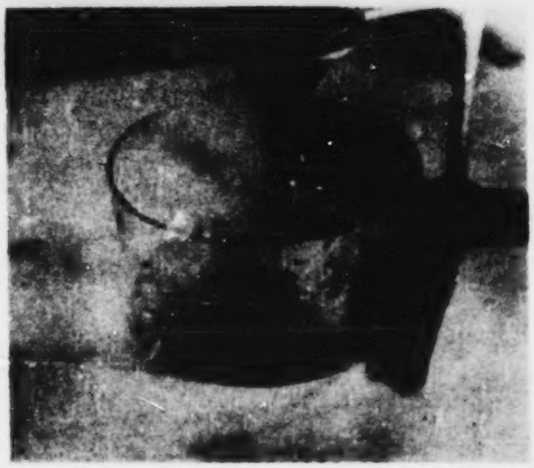

Figure 4. Polybutadiene Coated Residue of Sludge 700

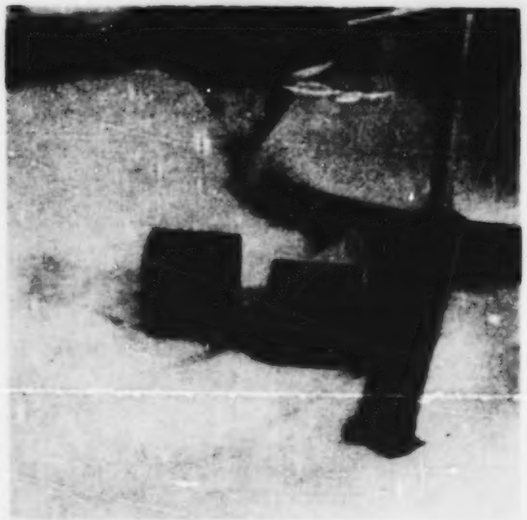

Figure 5. Fused Residue of Sludge 700

Method of Waste Agglomerating and Encapsulating

A pictorial sequence of the laboratory procedure employed for fabricating encapsulated heavy metal wastes is provided. The free flowing resin coated particulates are placed into a mold (Figure 6).

Figure 6. **Agglomerated Hazardous Waste Residue Emerging from Mold**

Agglomeration of the particulates placed under moderate mechanical pressures occurs in the temperature range of 250 to 400°F at various time intervals after the resin coating operation. Here demonstrations were sought which showed different wastes readily agglomerating over a wide temperature range from free flowing resin coated waste particulates stored at various time intervals.

Next the agglomerates are coated with powered polyethylene (Figures 7, 8, 9, and 10).

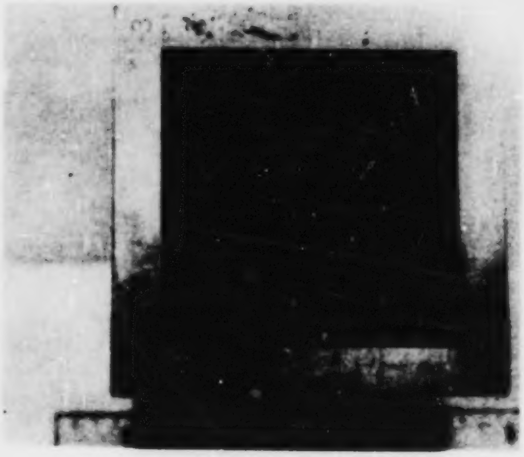

Figure 7. Hazardous Waste Agglomerate Positioned for Resin Jacketing

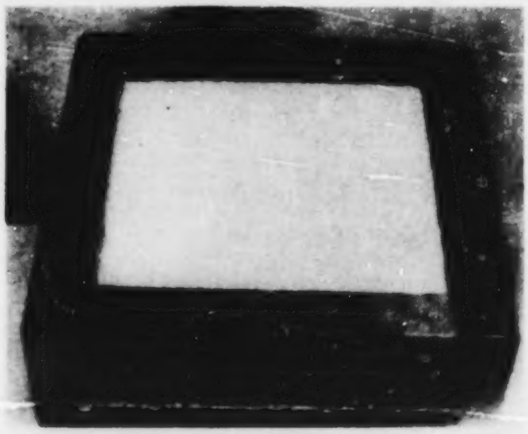

Figure 8. Agglomerate Submerged in Powdered Polyethylene

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Figure 9. Non-Jacketed Side Seen on the Free-Standing Agglomerate After the First Jacketing Step

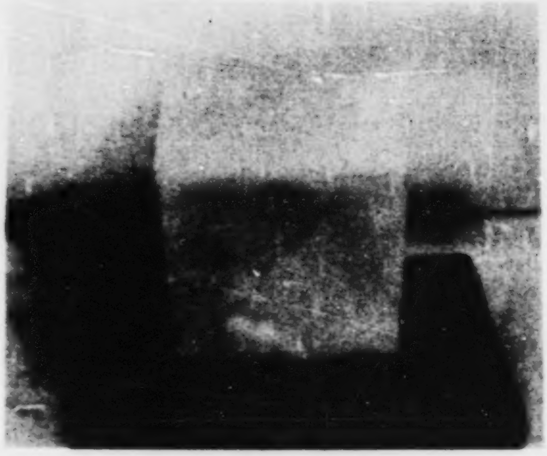

Figure 11. Encapsulated Agglomerate Seen After Final Resin Jacketing Step

Figure 10. Non-Jacketed Side of Agglomerate Seen Positioned for Final-Resin Jacketing

Figure 12. View of Cross Section of Encapsulated Hazardous Waste

Inspections of the encapsulated waste-binder agglomerates showed that the jackets adhered intimately and tenaciously to the agglomerates (Figures 11, 12, and 13).

Figure 13. Cross View of Encapsulated Arsenic Containing Waste

WASTE IDENTIFICATION

Wastes available for evaluating the polymeric process consisted of ten sludges (Table 1). These sludges were made available from a study being conducted for SHWRD by the U.S. Army Corps of Engineers, Waterways Experimental Station, Vicksburg, Mississippi.*

Another waste from the pesticide manufacturing industry became available during the study and was included. The waste contained 1-1/2 percent (by weight) monosodium methane-arsenate, 49 percent sodium chloride and 49 percent sodium sulfate (Figure 13).

Selection of Waste

The wastes selected were those designated in Table 1 as 200, 300, 500, 700, and 900. These materials differ significantly in chemical composition and material consistency. Furthermore, they represent a broad spectrum of sources in the chemical industry, each source issuing significant quantities of waste. A blend of equal parts by weight of 200, 300, 500, 700, 800, and 900 were encapsulated for detailed leaching and mechanical property studies. The blend contained the following atoms: Cu, Cr, Zn, Ni, Cd, Na, Ca, Fe, Hg.

The waste with monosodium methane-arsonate was also selected for evaluating the encapsulation process. The arsenic contaminant, existing as a sodium salt in a mixture of sodium salt compounds, is expected to be very water soluble. As such, test specimens from this material were judged to provide an excellent measure of the ability of the encapsulation method to isolate such wastes.

TABLE 1. WASTES AVAILABLE FOR PROCESS EVALUATIONS

Code No.	Source	Major Contaminants
100	SO_x scrubber sludge, lime process, eastern coal	Ca, $SO_4^=/SO_3^=$
200	Electroplating sludge	Cu, Cr, Zn
300	Nickel - Cadmium battery production sludge	Ni, Cd
400	SO_x scrubber sludge, limestone process, eastern coal	Cu, $SO_4^=/SO_3^=$
500	SO_x scrubber sludge, double alkali process, eastern coal	Na, Ca, $SO_4^=/SO_3^=$
600	SO_x scrubber sludge, limestone process, western coal	Ca, $SO_4^=/SO_3^=$
700	Pigment production sludge	Cr, Fe, CN
800	Chlorine production brine sludge	Na, Cl^-, Hg
900	Calcium fluoride sludge	Ca, F^-
1000	SO_x scrubber sludge, double alkali process, western coal	Cu, Na, $SO_4^=/SO_3^=$

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Cincinnati, Ohio 45268.

Waste Characterization

Five gallon quantities of aqueous sludges 200, 300, 500, 700, 800, and 900 were dewatered by exposure to the atmosphere to a consistency that exhibited no mobile water. The resulting residues were then heated in an oven at 300°F for about 1/2 hour. The residues thereafter granulated readily with mechanical stirring. A uniform consistency, absent of gross aggregates, was sought in particulation. No attempt was made to obtain a particular particle grind because various material consistencies were desired for agglomeration and encapsulation. Demonstrating successful passivation would indicate that it is not necessary to reduce wastes with different particulation characteristics to a specific grind, nor is it necessary to reduce a given waste repeatedly to the same grind. In some cases, mechanical stirring was not necessary. Residues of sludges 500 and 900 did not require stirring to obtain uniform material consistencies suitable for encapsulation.

The residues of sludges 200 and 700 appeared as agglomerated fines (Figures 14 and 15). The average dimensions of the agglomerates ranged between 5 to 15 mils. The monosodium methanearsonate containing waste appeared as grey-white in color and exhibited the consistency of sugar. It was processed as received without pretreatment.

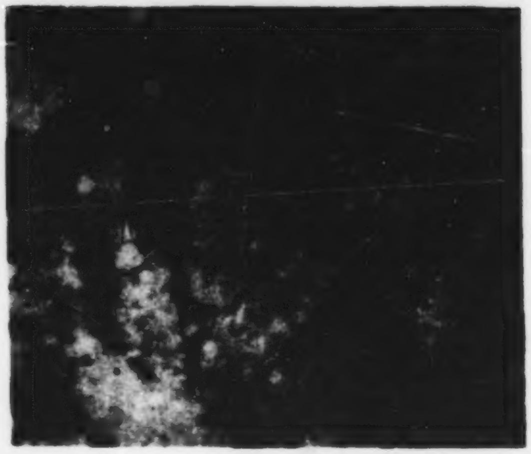

Figure 14. Waste 200 Residue (Electroplating Sludge) Magnification 100X, Scale Division 0.5 Mil

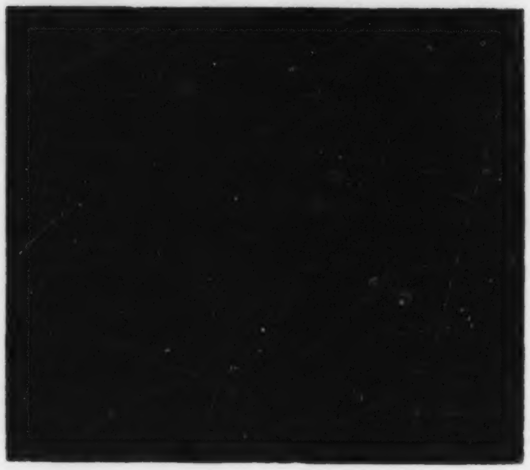

Figure 15. Waste 700 Residue (Pigment Production Sludge) Magnification 100X, Scale Division 0.5 Mil

PROCESS EVALUATION

Since the process was expected to provide adequate protection from toxic waste entering the environment, investigations included evaluation of the performance characteristics of the coated blocks of waste and polymers under various simulated environmental stresses. Although these tests were to be performed in the laboratory only, they were designed to provide indications of how well the coated waste-binder agglomerates would be expected to perform under actual disposal conditions such as the landfill, storage in deep mines, and the ocean.

Chemical (Leaching) Tests

The purpose of the chemical tests were to provide a measure of the effectiveness of the polyethylene jacket to prevent migration of the toxic components from the waste-binder (polybutadiene) agglomerate to the environment. Sixteen sample blocks of the waste were exposed to 8 different aqueous solutions: distilled water, 10% ammonium sulfide, 1.5 NHCl, 0.1 N citric acid, 1.25 N NaOH, 0.1 N NH OH, a simulated ocean solution, and 10% dioxane. These solutions were selected to expose the blocks to extremely harsh conditions, some of which would not normally be encountered in practice but which might represent a worse case condition. The blocks were immersed

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into the solutions for 120 days (Figure 16). Samples of the solutions were withdrawn on a periodical basis (1, 2, 5, 10, 20, 30, 45, 60, 90 and 120 days) and analyzed for selected components.

Figure 16. Encapsulated Wastes Specimens Under Aqueous Solutions

The concentration effects involved because of sample withdrawal were considered when calculating the concentration of the cations over the sampling period. Details of procedures, analytical techniques, and results are available.* Summary results of the sample analysis for cations after 120 days immersion indicate the effectiveness of encapsulation to prevent release of the components to the environment (Table 2). Concentrations of the unencapsulated wastes are provided in the right column. Of particular interest are the results for the citric acid and HCl solutions, which represent good solvents for heavy metals.

High retention of the arsenic after 80 days immersion, contained in the encapsulated monosodium methane-arsenate also indicates the capability of the encapsulation process to effectively control the release of a wide range of potentially toxic components to the environment (Table 3).

TABLE 2. CONCENTRATIONS OF CATIONS (PPM) IN CHEMICAL TEST SOLUTIONS AFTER 120 DAY IMMERSION OF THE ENCAPSULATED WASTE SPECIMENS*

Solutions† Cations	Distilled H_2O		Ocean Water		NH_4OH		NaOH	
Cu	.006	0.33	.003	91.4	.036	414	.087	339
Cr	.012	325	.030	0.34	.003	711	.008	5,884
Zn	.015	.033	.007	1.50	.001	17.4	.021	15,519
Ni	.085	5.00	.004	0.40	.088	1.00	.068	0.2
Cd	.017	21.5	.042	984	.010	94.0	.016	1,500
Na	.218	5,334	-	-	-	-	-	-
Ca	.020	18,237	-	-	.016	23.0	.006	44.3
Hg	.001	.002	.002	1.05	.001	0.26	.0003	.005

*Under each leachate, left column, encapsulated wastes; right, unencapsulated.

†Solutions: distilled water, simulated ocean water, 0.1N NH_4OH, 1.25 N NaOH, 10% ammonium sulfide, 0.1N citric acid, 1.5N HCl, 10% dioxane.

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*Contracts 68-03-0089 and 68-03-2037. Solid and Hazardous Waste Research Division, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268. Final reports are in preparation.

TABLE 2. CONCENTRATIONS OF CATIONS (PPM) IN CHEMICAL TEST SOLUTIONS AFTER 120 DAY IMMERSION OF THE ENCAPSULATED WASTE SPECIMENS* (CONTINUED)

Solutions† Cations	$(NH_4)_2S$		Citric Acid		HCl		Dioxane	
Cu	.051	2.9	.010	1,803	.011	25,035	0.14	5.9
Cr	.009	233	.012	2,524	.035	127,390	.004	71.6
Zn	.114	.089	.008	18,270	.011	8,231	.004	1.6
Ni	.093	2,589	.055	4,719	.168	42,352	.002	5.5
Cd	.096	8.3	.052	6,401	.019	106,416	.037	19.5
Na	-	-	.035	6,085	.218	45,098	.610	4,834
Ca	-	-	.345	21,537	.013	590,650	.146	134.9
Hg	-	-	.0005	.004	.019	171.5	.0003	.002

*Under each leachate, left column, encapsulated wastes; right, unencapsulated.

†Solutions: distilled water, simulated ocean water, 0.1N NH_4OH, 1.25 N NaOH, 10% ammonium sulfide, 0.1N citric acid, 1.5N HCl, 10% dioxane.

TABLE 3. ARSENIC AND SODIUM CONCENTRATIONS (PPM) IN TEST SOLUTIONS

	Solution	Blank	Day 1*	Day 80	Uncapsulated Waste†	Comments
Arsenic‡						
	Distilled water	<.01	<.01	<.01	2,420	No arsenic detected
	1.5 N HCl	<.01	<.01	<.01	1,017	No arsenic detected
Sodium♦						
	Distilled water	.050 (±.002)	.191 (±.005)	.21 (±0)	10,685	No Na detected Values within Instrument noise
	Sodium	.002 (±.001)	.164 (±.001)	.176 (±.002)	10,919	No Na detected Values within Instrument noise

*Days samples immersed in solution.

†Values determined for 400 grams of unencapsulated waste in 1200 ml of leaching solution (equal to the encapsulated material).

‡Determined by the silver diethyldithiocarbamate method.

♦Determined by atomic spectroscopy.

Mechanical Tests

Tests were performed to evaluate the ability of the encapsulated waste-binder agglomerate to withstand mechanical stresses. These tests included measurements of compression strength, freeze-thaw resistance, impact strengths, puncturability, and a measure of the bulk density. Variations from standard testing procedures were required in some instances to accommodate the test specimens and because of scaling factors. Performance of the specimens, however, was high and is typified by the compressive strength at yield of approximately 1600 psi. Although grossly distorted, the jacket accommodated the distortion and retained the hazardous waste (Figure 17). Blocks exposed to freeze-thaw cycles ruptured at approximately 1300 psi. The density of the agglomerates tested were 90 to 100 lbs/ft.

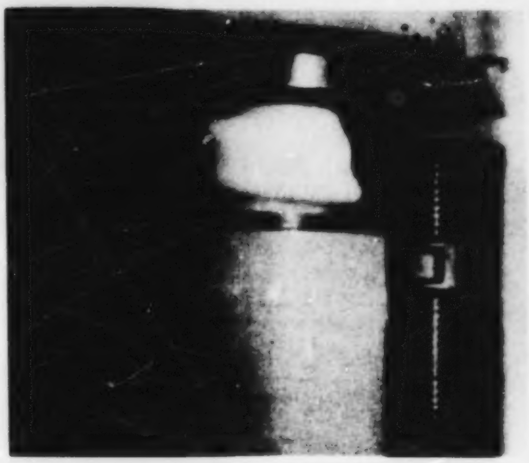

Figure 17. Distortion Mode of Encapsulated Hazardous Waste Under Unidirectional Mechanical Pressure

Process Design

Engineering study yielded a process flow sheet, a potential plant design, and provided estimated costs for fabricating production scale encapsulated waste products. This study characterized the production products as follows: dimensions, cubic, approximately two feet on edge; weight, in the range 800 to 1000 pounds; jacket, about 1/4 inch thick polyethylene resin; encapsulate, hazardous waste agglomerate cemented by 3 to 4 percent w/w polybutadiene resin.

The cost was estimated at $91 per ton dry waste at 20,000 tons per year throughput. Studies relating cost to various parameters indicated that the most cost sensitive area was the cost of resins, accounting for approximately 50 percent of the total cost. The cost was based upon the price of commercial resins, but "crude" and/or scrape resins appear to be applicable, especially polybutadiene. Consequently, potential exists for significant reduction of cost.

Details of the suggested process, including mass and energy balances are available.

CONCLUSIONS

Results of the study and evaluations described in this paper led to the following conclusions:

- Polybutadiene resin is an effective medium for producing hazardous waste-binder agglomerates containing 94 to 97% by weignt of waste.
- Waste-binder agglomerates can be securely encapsulated with 1/4-inch thick polyethylene jackets by fusing powdered polyethylene onto agglomerate surfaces, yielding passivated hazardous waste.
- Based upon process performance under laboratory chemical and mechanical stress tests, the encapsulation of waste-binder agglomerates would be expected to provide a high degree of control over the release to the environment of unwanted quantities of the hazardous waste tested.
- Difficult to manage hazardous waste containing constituents such as sodium metaarsenate and arsenic trisulfide were assessed to be amenable to control by the polymeric encapsulation process described in this paper. Based upon the process evaluations and associated assessments, the process appears to be compatible with a wide range of hazardous waste which may not be adequately manageable by other techniques.
- The process as designed is expensive; estimated at $91 per ton of dry waste for a plant processing 20,000 tons per year. Commercial resins were determined to account for more than 50% of the product production costs. However, studies suggest that these costs can be significantly reduced by use of crude or scrap resins.

RECOMMENDATIONS

Additional study is recommended to evaluate large production scale blocks (800 lbs) of encapsulated hazardous waste-binder agglomerates under actual field disposal conditions. Engineering design modifications, as well as evaluations of less costly crude resins, are required to provide a less costly process.

The process as described appears to be costly in comparison to other available techniques for managing hazardous waste. Assessments are required, however, to better define the costs of the process versus its potential ability to manage hazardous waste that other processes may not control within environmentally acceptable levels. For such cases, costs of the process will become of secondary importance.

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AN EVALUATION OF STORING NONRADIOACTIVE HAZARDOUS WASTE IN MINED OPENINGS

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ABSTRACT

An assessment was made of the technical feasibility of storing nonradioactive hazardous wastes in underground mined openings. Since environmental protection was the most important concern, basic criteria were established which had to be met before the concept could be considered technically feasible. These basic criteria were established so that a maximum level of environmental protection could be assured and the potential for hazardous wastes stored underground to be carried from the mine in either air or water would be minimized. These criteria include: geologic stability in and around underground facility; hydrologic and surface isolation; chemical compatibility of the stored wastes with each other and the host medium; personnel safety; underground mining regulations and restrictions; and long term flexibility to meet changing conditions. The results show that a majority of the wastes considered can be stored underground in an environmentally acceptable manner if they are properly treated and containerized. Various mine environments in the United States are applicable for such storage; room and pillar mines in salt, potash, and gypsum appear to be the most favorable. Although the underground storage and management of hazardous industrial wastes is both technically feasible and environmentally sound, further and more detailed research, including an economic evaluation, is recommended.

INTRODUCTION

This paper deals with the concept of using underground mined openings in salt and other media as a respository for nonradioactive hazardous wastes. An assessment was made of the technical feasibility from an environmental point-of-view. Throughout the study, the prime considerations were an assessment of the potential effects on the environment and that storage of the hazardous wastes would be accomplished in such a manner that associated environments were not harmed.

The concept of using underground cavities as disposal sites for hazardous wastes is certainly not unique. The United States Atomic Energy Commission conducted intensive investigations of storing radioactive wastes. Although found feasible, some technical uncertainties related to the actual waste storage concept and socio-type problems prevented implementation of the concept (1). This is not true in the Federal Republic of Germany where the Asse Salt Mine began processing and disposing of low-level radioactive waste in April of 1967. Intermediate level radioactive waste was accepted in August of 1972, and test disposal of solidified high-level radioactive waste is scheduled for 1976-1977 (2).

There are no known underground mines processing and storing hazardous (nonradioactive) waste in the United States. However the similarity of problems of storing hazardous wastes to those of storing radioactive wastes has been recognized. Germany began consideration of the concept in their June 1972 Federal Waste Removal Law. Review of selected provisions of that law indicate that parties engaged in mining operations or the operator of a mineral extraction enterprise may be "obligated" by an "appropriate authority" to "tolerate the elimination" of wastes in cleared-out sections of his facility and to make the facilities available for such purposes. As a result, some enterprising companies, after meeting certain legal requirements and receiving Government approval, began to offer and promote the service of underground storage and disposal of toxic chemical wastes (3).

The problems of increasing quantities of industrial and other wastes containing toxic components and their associated management (or mis-management) has been documented (4). Technologies have been identified which offer acceptable treatment alternatives for selected hazardous wastes (5). In many cases the wastes can be reduced to nontoxic materials. However, we must recognize that technologies are not available to reduce all toxic wastes to nontoxic forms. Therefore, alternative techniques must be investigated and developed to manage these toxic residuals. The study discussed in this paper was conducted as a portion of a broader Federal program directed at assessing technologies available and potentially available for treating and managing hazardous wastes (6).

The use of underground space in salt deposits for the long term retention of hazardous waste is considered a very promising candidate technique for managing toxic residuals. The study discussed in this paper further explored the concept. Although salt appeared to be the best candidate, other media were considered.

Since the overriding study considerations were environmental concerns, basic criteria were established which had to be met before the concept could be considered technically feasible. These basic criteria were established so that a maximum level of environmental protection could be assured and the potential for hazardous wastes stored underground to be carried from the mine in either air or water would be minimized. These criteria include: geologic stability in and around an underground facility; hydrologic and surface isolation; chemical compatibility of the stored wastes with each other and the host medium; personnel safety; underground mining regulations and restrictions; and long term flexibility to meet changing conditions.

As an added incentive to assure the application of strict criteria to the study, and for socio-related reasons, the study team adhered to a basic philosophy developed early in the study. This philosophy involves the concept of controlled storage rather than disposal of the waste. The latter connotates placement of waste in the mine with little or no subsequent control of its disposition; similar to the "open dump". The former is proposed to permit emplacement of the waste for both short and long-term retention under engineered and controlled conditions. The waste disposition would be continually monitored and if determined necessary because of impending problems, transferred from one site to another. Also, in the event of future changes in technology, or for appropriate economic incentives, selected wastes would be available for recovery and redistribution for useful purposes.

PROBLEM DEFINITION

Investigations Required

Assessment of the environmental acceptability for storing hazardous waste underground involved the following investigations:

- o The development of geological criteria which can be used to select those sites providing maximum environmental protection for the emplacement of hazardous industrial wastes.
- o The characterization of hazardous industrial wastes to determine if they could be placed in underground mines in an environmentally acceptable manner.
- o The determination of the potential for wastes to migrate from the mine environment.
- o An evaluation of the capability of existing equipment to detect, monitor, and control potential waste contamination and migration.
- o An evaluation of mine design, construction, and operating requirements necessary to ensure safe operation and complete environmental protection.

Although not within the scope of this study, additional work is being initiated to determine economic feasibility.

Approach

Based upon the primary objective of assessing the environmental acceptability of the concept, the study was divided into the following major tasks (Figure 1):

- Problem Definition
- Geological Characterization
- Waste Characterization
- Geochemical Assessment
- Detection, Monitoring, and Control Technology
- Regulations Assessment
- Mine Design
- Conclusions

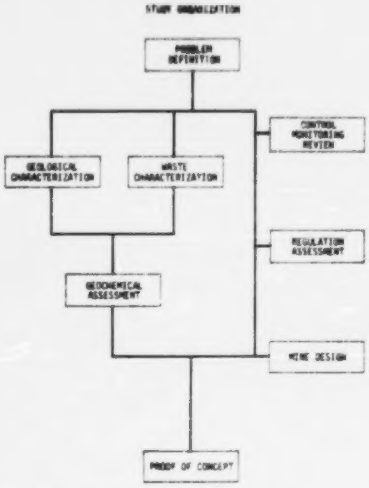

Figure 1. Study Organization

A concurrent review of the available literature pertaining to underground mines, subsurface disposal problems, industrial waste streams, and current waste disposal or storage techniques identified three major problem areas concerning waste isolation:

- The physical and geological environment of an underground storage facility.

- The chemical and hazardous nature of the wastes.

- The geochemical compatibility of the wastes with mine environments.

These were considered to be of primary concern in determining the environmental acceptability of the concept. However, to provide a more realistic assessment of the concept, it was also necessary to evaluate the following:

- Detection, monitoring, and control technology.

- Regulatory aspects of waste storage in mines.

- Design of an underground waste facility.

Although important, the economic aspects of this storage concept were not directly addressed. However, in approaching each area of the study, broad economic considerations were often unavoidable when choosing one alternative over another.

MAJOR STUDIES

Geology and Mine Selection Criteria

Lithologies

Basic lithologies for evaluation were selected on the basis of known characteristics and physical occurrence. Salt, having received the greatest previous attention as a waste disposal medium, was of primary interest. Other evaporites (gypsum and potash) were investigated due to their similarity, occurrence, and development. Other lithologies were selected on the basis of their proven storage potential of hydrocarbon products, geographic occurrence, minability, and general characteristics.

Limestones were considered because they occur in many areas of the United States, are often mined, and appeared to satisfy many of the geologic and mine criteria. In addition, by determining the suitability of limestone, other related lithologies would also be indirectly considered. The most important of these is dolomites which are generally stronger, commonly mined, and widely distributed.

Shales were chosen because of their widespread occurrence and potential for beneficial reactions (ion exchange capacity) with the wastes. Although not commonly mined, shales are generally impervious and have been successfully used for the storage of liquid petroleum products.

Granite is less uniform (homogeneous) than the other selected lithologies and is not typically mined by room and pillar methods. It is also often associated with mountainous terrain. On the other hand, it is a very competent lithology and is essentially impervious except where locally fractured. It does not weather easily, which implies little reactivity to weathering agents, occurs in large geographic areas, and has been mined by room and pillar methods for hydrocarbon storage.

Selection of candidate lithologies recognized that general characterizations are not wholly practical or realistic. However, to meet the study objectives, certain generalizations were required. The lithologies considered in this study are believed to be the most promising. This list, however, is not restrictive and other lithologic environments could be added as required.

Preliminary Decision Model - Waste Storage Mines

To facilitate the evaluation of lithologic environments and mined openings, a preliminary decision model was developed (Figure 2). Using this model, it is possible to screen any mined environment for preliminary suitability. By subjecting all potential underground storage sites to this screening technique as information becomes available, it will be possible to arrive at a listing of the most promising sites. These sites can then be further evaluated and subjectively compared.

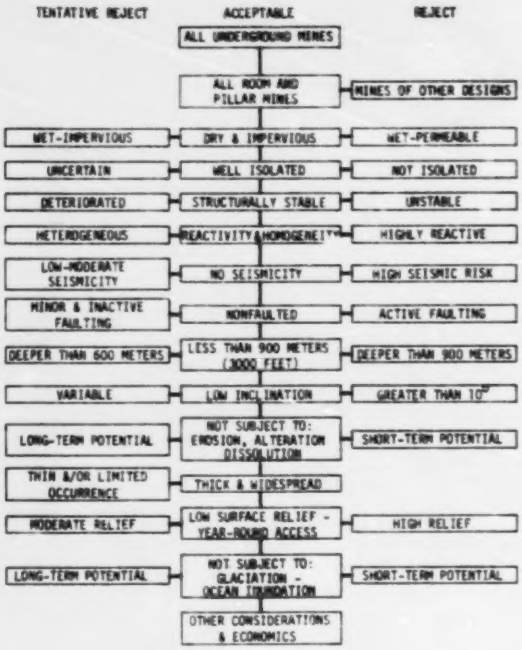
TENTATIVE REJECT
ACCEPTABLE
REJECT
ALL UNDERGROUND MINES
ALL ROOM AND PILLAR MINES
MINES OF OTHER DESIGNS
WET-IMPERVIOUS
DRY & IMPERVIOUS
WET-PERMEABLE
UNCERTAIN
WELL ISOLATED
NOT ISOLATED
DETERIORATED
STRUCTURALLY STABLE
UNSTABLE
HETEROGENEOUS
REACTIVITY & HOMOGENEITY
HIGHLY REACTIVE
LOW-MODERATE SEISMICITY
NO SEISMICITY
HIGH SEISMIC RISK
MINOR & INACTIVE FAULTING
NONFAULTED
ACTIVE FAULTING
DEEPER THAN 600 METERS
LESS THAN 900 METERS (3000 FEET)
DEEPER THAN 900 METERS
VARIABLE
LOW INCLINATION
GREATER THAN 10°
LONG-TERM POTENTIAL
NOT SUBJECT TO: EROSION, ALTERATION DISSOLUTION
SHORT-TERM POTENTIAL
THIN &/OR LIMITED OCCURRENCE
THICK & WIDESPREAD
MODERATE RELIEF
LOW SURFACE RELIEF - YEAR-ROUND ACCESS
HIGH RELIEF
LONG-TERM POTENTIAL
NOT SUBJECT TO: GLACIATION - OCEAN INUNDATION
SHORT-TERM POTENTIAL
OTHER CONSIDERATIONS & ECONOMICS

Figure 2. Preliminary Decision Model - Hazardous Waste Storage Mines

Geochemical and Waste Characterization Analysis

Acceptability of Waste for Storage Underground

Characterization of the wastes concerned determining the environmental acceptability of the wastes for underground storage. This determination was approached from three main viewpoints:

- An investigation of the physical, chemical, and hazardous properties of the wastes to assess their acceptability for underground storage before and after treatment.
- The control of possible environmental contamination through proper treatment and containerization.
- An investigation of possible environmental degradation which may occur after storage from the chemical interaction of the wastes with each other and with the geological formations or from waste migration.

Until very recently, studies have been primarily concerned with identifying and analyzing the most hazardous constituents in waste streams rather than a total waste stream analysis. This type of analysis has been called the "pure-form" approach and assumes the properties of a waste stream to be identical to those of its most hazardous constituent. Although the most realistic characterization of wastes will require a complete waste-stream analysis, it was necessary to use the "pure-form" approach due to the lack of available information on total waste streams. However, the methodology for analysis that was developed can be applied equally well to either "pure-form" wastes or waste-streams. As additional waste-stream data are obtained, new candidates for storage in underground mines can be realistically screened using the developed methods.

During the EPA evaluation of the hazardous waste problem 115 wastes were identified as special problems, and were recommended for disposal in National Disposal Sites (NDS)(7). These were considered as the candidate wastes for storage in a mined facility.

The waste characterization method developed consists of the following steps:

- o Compile and present the physical and hazardous properties for the wastes of concern.
- o Define and establish the criteria for "ideal" waste form for underground storage.
- o Develop a Hazard Index rating of the wastes to indicate their acceptability as candidates for underground storage without pretreatment (Figure 3).
- o Screen and divide the wastes according to their Hazard Index into those which require:
  - a. no pretreatment
  - b. optional pretreatment
  - c. mandatory pretreatment
- o Compile and present the best waste treatment procedures available for rendering the wastes to their most ideal form for underground storage.
- o Further screen and divide the wastes into those which:
  - a. are acceptable for underground storage without pretreatment
  - b. must be treated and whose treatment products are toxic, but acceptable for underground storage
  - c. must be treated and whose treatment products are essentially nontoxic, but acceptable for underground storage
  - d. must be treated and whose treatment requires further study
  - e. are unacceptable for underground storage in any form.
- o Define and explain any potential reactions that could occur between the stored wastes after they are in place in a mine.
- o Define and explain any potential reactions that could occur between the stored wastes and the receiving geological formations.
- o Assess the potential for migraton of the wastes.

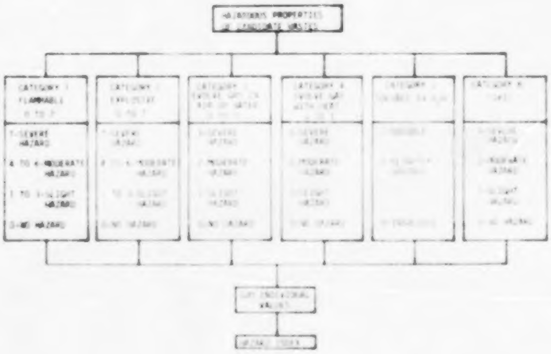

Figure 3. Hazard Index of Candidate Wastes

The environmental acceptability of a hazardous waste underground depends upon the level of hazard it presents prior to storage. A waste must be evaluated with respect to potential effects on the biosphere resulting from its handling, treatment, storage, or possible migration. If it was found that a waste was too hazardous to the environment in its pure form, then its hazards could, in most cases, be reduced through treatment. The treatment procedures, as presented in the study report, are theoretical in nature.

It was assumed that each waste would be containerized for storage. This assumption was based upon many factors. From an environmental standpoint, the containerization of the wastes would provide maximum safety during handling and storage while minimizing the potential for contamination of the biosphere through migration. In addition, if it became feasible to recycle a waste or an environmental calamity was eminent, containerization would allow a waste to be retrieved from storage without danger. For these reasons, it was concluded that hazardous wastes should be stored in mines according to the Bureau of Mines safety requirement 30 CFR, Chapter 1, part 57, 16-4 which reads as follows: "Mandatory - Hazardous materials shall be stored in containers of a type approved for such use by recognized agencies; such containers will be labeled appropriately."

Waste Interaction

Once a waste has been placed underground, the possibility of environmentally hazardous compounds being formed by chemical reactions among the stored wastes must be assessed. It was assumed that, in the event of a mine flood, the containers would rupture allowing the wastes to go into solution. Although this situation could be prevented by proper treatment and containerization, the "worst case" philosophy was employed. Under these conditions, the number of potential chemical reactions is staggering. Due to the enormous number of possible reactions, consideration of only the immediate or first level reactions was within the scope of the study.

In an attempt to evaluate the types of reactions which might occur, a waste interaction matrix utilizing the "Acceptable Form" was developed.* The "Acceptable Form" of a waste can be defined as the waste which has been treated to its lowest level of toxicity or hazard so that it approaches the following guidelines:

- Nonflamible
- Nonexplosive
- Will not evolve hazardous gases when exposed to air, water, or heat
- Containerized
- Unable to be dispersed in air or water in concentrations exceeding the established TLV for the material

The reactions are then described as hazardous and nonhazardous. A hazardous reaction is one in which either of the following might occur:

- Potential for migration of a waste is increased by the formation of a more soluble toxic compound.

- New substances are formed which present greater hazards to the environment than the original substances.

Geochemical Interaction and Compatibility

Since environmentally unfavorable reactions may occur for the chemical interaction of the stored wastes with the receiving geological formations, an evaluation of this was a necessary step in determining the environmental acceptability of the concept. An unfavorable reaction would be one in which any of the following might occur:

- The potential for migration of a waste is heightened by an increase in its solubility through complexing or ionization.

- The structural integrity of the lithology is unfavorably altered.

- Any new substances are formed which present greater hazards to the environment than the original substances.

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*EPA Contract 68-03-0470, Solid & Hazardous Waste Research Division, Environmental Protection Agency, Cincinnati, Ohio 45268. Figures and details of the waste interaction matrix are too complicated for reproduction in this paper.

In a favorable reaction, the reverse of the above would be true. If an unfavorable reaction occurs, a waste is said to be incompatible in a lithology. If a favorable reaction or no reaction occurs, a waste is said to be compatible in a lithology.

The lithologies which were selected as candidate formations for storage are:

- o Rock salt (Halite)
- o Gypsum
- o Potash (Sylvite)
- o Shale (1) (Relatively high montmorillonite content)
- o Shale (2) (Relatively low montmorillonite content)
- o Limestone
- o Granite

For the purposes of this analysis, it was assumed these lithologies were homogeneous in composition and that any impurities normally found within them would not occur in amounts sufficient to alter the basic reactions between the wastes and the lithology.

In this investigation, the "worst case" analysis was again employed. The storable wastes were assumed to be in contact with the selected lithologies under both wet and dry conditions. These conditions would not be possible unless the waste containers were ruptured by some calamity such as flooding. The reactions resulting from the interaction of the wastes and receiving formations could be controlled through proper treatment and containerization. However, this analysis was necessary to ensure the appraisal of all conditions which might adversely affect the environment.

Projected Waste Volumes

The last step in evaluating the wastes as candidates for underground storage is to investigate their probable volumes. This is important in order to obtain some idea of the magnitude of the problem of waste disposal and to assess mined storage as a potential answer. Previous studies have estimated waste volumes and established a relationship between population concentration and volume of waste generated.

Waste Migration

The primary result of the investigation of the potential environmental effects of waste migration is that migration can be avoided if the proper techniques of waste treatment and containerization are employed. Two principle methods by which a waste may migrate from the mine are to be carried by ground water and by reacting with host rock. Both of these are dependent upon the solubility of a waste. Therefore, decreasing the solubility of a waste during treatment should be of major concern. Since the goal of underground storage is the complete isolation of the hazardous wastes from the biosphere, the potential migration of the wastes must be controlled. Perhaps the best method of avoiding migration is through the use of containers. If a stored waste is never allowed to contact the mine environment, there would be no chance of it escaping. One disvantage of containers is that their use could become economically prohibitive.

A reasoning sequence was used to analyze each waste for its acceptability for storage underground (Figure 4). This aid was developed to help insure that study criteria were properly considered. It provides a review of the assessments made to determine the acceptability of wastes that are candidates for underground storage.

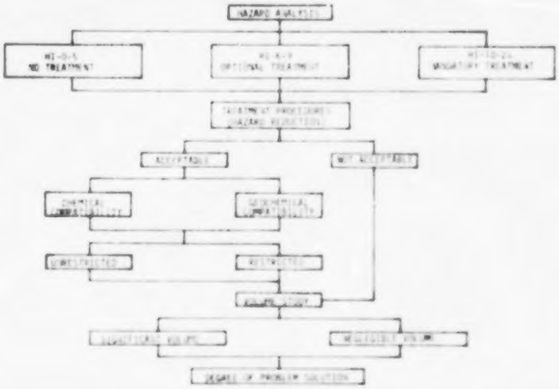

Figure 4. Simplified Waste Characterization Analysis Flow Diagram

Detection, Monitoring and Control

The emplacement, storage, and management of noxious chemical wastes in underground mined openings will require continuous surveillance of the mine opening, contiguous subsurface areas, and surface environments. The implementation of detection monitoring and control systems will help insure isolation and safety by providing early warning of contamination in air and water and will also allow early detection of structural fatigue. By these means the potential for waste interaction with the biosphere can be strictly controlled.

The basic requirements of a detection, monitoring, and control system will include the following:

- Continuously monitor, sample, and clean the circulating mine air.
- Provide immediate response (alarms, etc.) to critical changes.
- Indicate long-term finite changes.
- Allow source area identification.
- Provide qualitative and quantitative analysis of contaminants in air and water.
- Provide high reliability.
- Be adaptable to change and improvement as the technology advances.
- Provide decontamination capability.
- Allow recovery and storage of released wastes.

The importance of monitoring the short and long-term structural integrity of a mine used for housing hazardous wastes involves several aspects of this storage concept. Of immediate interest is the safety of personnel working in the facility. Such things as roof falls and slabbing are hazards which can normally be prevented by good maintenance practices. Hazards of a larger consequence would result if such failures were to rupture containers. If this occurred, not only would mine personnel be put in jeopardy, but the entire waste facility might be lost temporarily, or even permanently. To guard against such an occurrence, mines must be selected with high regard to stability; and to provide additional insurance, various monitoring instruments and techniques should be implemented. Instruments which are presently available can provide finite measurements of short and long-term changes and thus allow preventative measures to be taken before failure occurs.

The hydrologic environment in the area of an underground hazardous waste storage facility will require monitoring to assure isolation of the wastes and protection to the environment. Streams, springs, and wells in the vicinity can be physically sampled using standard methods and the samples then analyzed in a laboratory.

Regulation Assessment

Many existing laws and regulations are related to hazardous and potentially hazardous substances that could affect the quality of our environment. The objectives of these laws are, in general, to improve the quality of the environment and to protect it from further pollution by establishing national standards. Some of these laws are related to disposal of waste products, however, no laws or regulations were found to directly govern the disposal or storage of nonradioactive hazardous waste products in underground salt deposits and/or mined openings.

ADDITIONAL MINE CONSIDERATIONS

The concept of long-term storage of hazardous industrial wastes in underground mines appears feasible and might be preferred to surface storage for several important reasons. Among these are:

- It is well protected.
- It provides permanent, very long-term containment.
- Valuable surface area is not used.
- It provides good security and control of access.
- It requires a minimum of maintenance.
- Storage space can be continuously expanded.

- There is less chance of damage to the environment in case of a spill.
- The facility could possibly be designed to survive a nuclear blast.
- It is protected from the ravages of the weather.
- A nearly constant temperature exists underground.
- Humidity would not vary excessively.
- The waste would be out of sight.
- It is less subject to sabotage.

There are many different types of mines existing today that have been excavated using numerous mining methods. Of the many mining methods in use, the room and pillar method appears to be best suited to the storage of wastes underground. The room and pillar method consists of mining a number of parallel rooms (drifts) in the formation and connecting them by means of another series of parallel rooms (crosscuts) mined at right angles to them. The room and pillar mining method is generally reserved for deposits that can be mined nearly horizontal.

Some advantages of the room and pillar mine as opposed to other types that could be used for hazardous waste disposal include:

- The mine layout is usually near horizontal or has a low dip with the underground workings generally all on one level. In most cases the grade is shallow enough to permit the use of rubber tired equipment.
- The rooms are generally large.
- Large equipment can be used if required to handle heavy or bulky loads.
- The mine is relatively simple to excavate.
- The mining plan provides for considerable flexibility in overall layout.
- Mine ventilation is simplified.
- Mine haulage is simplified.

A preliminary assessment was made of the relationship between the location of potentially suitable underground mines to the volume of hazardous industrial waste generated. It is clear that every region where significant quantities of waste are generated contains at least a few operating mines in the selected lithologies. Several of these mines can be expected to meet the criteria for hazardous waste storage.

Waste Handling Procedure

The overall operation of the storage facility must be well planned and coordinated. The more important operations of a hypothetical hazardous waste storage facility is described in order to point out key operations.

The waste material, as received at the storage site, may be in a storage container and a form suitable for final storage. On the other hand, it may be more economical to ship the waste in large, bulk tank cars to the storage site where it would then be transferred to smaller containers for permanent underground storage. Economics or other conditions may also dictate that some of the waste products be reprocessed at the storage site prior to being permanently containerized and stored. These are variables that would have to be considered in the final design of a hazardous waste storage facility.

Once the waste has been received at the site, careful inventory controls must be maintained at all times. This is necessary in order to keep close check on the waste reprocessing and recontainerizing, if any, and to verify that each given waste product is stored in the proper storage cell underground. A flow diagram was developed to illustrate the possible waste handling steps (Figure 5). The health and safety staff would monitor the waste handling processes from the time the waste arrives at the site until it is safely stored underground.

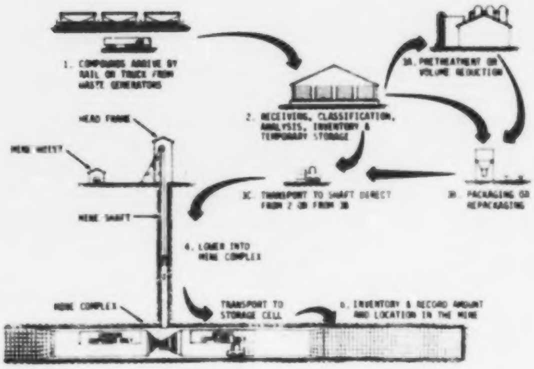
1. COMPOUNDS ARRIVE BY RAIL OR TRUCK FROM WASTE GENERATORS
2. RECEIVING, CLASSIFICATION, ANALYSIS, INVENTORY & TEMPORARY STORAGE
3A. PRETREATMENT OR VOLUME REDUCTION
3B. PACKAGING OR REPACKAGING
3C. TRANSPORT TO SHAFT DIRECT FROM 2 OR FROM 3B
HEAD FRAME
MINE HOIST
MINE SHAFT
4. LOWER INTO MINE COMPLEX
MINE COMPLEX
TRANSPORT TO STORAGE CELL
6. INVENTORY & RECORD AMOUNT AND LOCATION IN THE MINE

Figure 5. Waste Handling Flow Chart

CONCLUSIONS

The following conclusions are based upon the assessments made during this study:

- Storage in underground mines is an environmentally acceptable method managing hazardous industrial wastes provided the recommended procedures of site selection, treatment, containerization, and waste handling are followed.
- Environmentally suitable underground space for the storage of hazardous industrial wastes now exists within the United States.
- Room and pillar mines in salt, potash, and/or gypsum offer the most suitable containment with respect to the study criteria.
- The first-level chemical interaction of storable hazardous industrial wastes with each other or with the receiving geological formations will not create any uncontrollable situations.
- The potential for waste migration out of a properly selected mine is slight and can be controlled through proper treatment, containerization, and site selection.
- **Systems adequate to detect, monitor, and control waste migration can be developed from current technology.**
- **A need for legislation concerning the storage of hazardous industrial waste in underground mines is indicated.**
- **The design and operation of an underground storage facility for hazardous industrial wastes is technically feasible.**
- **Locating regional waste storage facilities at existing mines is technically feasible.**

DISCUSSION AND RECOMMENDATIONS

Procedures were developed to assess selected lithologies as environmentally acceptable storage sites for nonradioactive hazardous waste. These procedures are applicable to the evaluation of specific sites. Once identified as a candidate storage site, detailed physical and geological evaluations of the mine should be conducted using the criteria and techniques outlined. In a like manner, because of the unique physical nature of each mine, the potential for waste migration from each specific site should be assessed even though migration is considered unlikely.

The concept appears technically feasible. Economic feasibility, however, has not been determined and should be before performing additional technological evaluations.

Throughout the study, decisions to either accept or reject waste for underground storage, or for accepting or rejecting lithologies, or for similar matters, were based upon strict and demanding criteria aimed at providing maximum protection to the environment. If a waste were judged to be unacceptable for storage based upon its hazard rating, it was rejected. In reaching such decisions, no attempt was made to judge the relative degree of hazard of storing the waste underground as opposed to some other disposition. For some waste, storage underground may be the test alternative management technique available. In addition, further evaluations may determine that the technical criteria established for accepting

or rejecting waste for storage are too restrictive. This would only increase the concept's potential as a safe management technique for nonradioactive hazardous waste.

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EVALUATION OF SELECTED SORBENTS FOR THE REMOVAL OF CONTAMINANTS IN LEACHATE FROM INDUSTRIAL SLUDGES

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ABSTRACT

This paper presents the laboratory results of the evaluation of ten natural and synthetic materials (Bottom Ash, Fly Ash, Vermiculite, Illite, Ottowa Sand, Activated Carbon, Kaolinite, Natural Zeolites, Activated Alumina, Cullite) for the removal of contaminants in the leachate and liquid portion of three different industrial sludges (Calcium fluoride sludge, Petroleum sludge, Metal finishing sludge). This investigation involves beaker studies to evaluate the static absorption capacity of sorbent materials using maximum background concentrations of contaminants in the leachate; followed by lysimeter studies to obtain information regarding the dynamic absorption capacity and permeability characteristics of these materials. The analysis of the leachate involves the determination of pH, conductivity, residue, chemical oxygen demand (COD) total organic carbon (TOC), anionic species, and cationic species before and after contact with sorbent materials. The results of the beaker studies show that there is no single sorbent of those examined that can significantly reduce the concentration of all the constituents in a leachate to acceptable levels. Initial results using the lysimeters, confirm these findings. The results however, indicate that combinations of different sorbents can be used to reduce all the contaminants in the leachates obtained from a specific sludge to acceptable levels. The selection of the combination of sorbents to treat a given leachate depend upon the sludge and contaminants in the leachate.

INTRODUCTION

As a result of the establishment under the Federal Water Pollution Control Act of 1972 of a no pollutant discharge policy to receiving waters by 1985, industry will be faced with finding feasible techniques for the safe disposal of hazardous and toxic sludges generated during the treatment of their industrial waste streams. In the main, the most often used sludge disposal technique for industrial sludges has been sanitary landfills. Some progress has and is being made in the development of closed-loop type waste treatment, however, this technology is not expected to significantly reduce the sludge volume in the near future. The disposal of industrial sludge in landfills can, however, lead to contamination of ground and surface waters by the pollutants in the liquid portion of these wastes. Also, pollutants may be transported to the ground or surface water as a result of ground water infiltration or rainwater percolating or leaching through the landfill (1).

At present, there is a lack of means to accurately predict the leaching potential, and direction and rate of flow of the leachate through the soil surrounding the landfill site(2). These problems could be overcome by isolating the landfill site from its immediate soil surroundings. By lining the base and sides of the landfill with compacted low impermeable loess soil, horizontal groundwater movement of the leachate is prevented (3). Polyvinyl chloride and butyl rubber liners have also been used for this purpose (4)(2). This however, creates a "bath tub without a drain" unless the rainwater that percolates down through the landfill is provided a means of escape. This could be accomplished using gravity outlets such as drainage tiles or perforated corrugated metal pipe installed in the lowest portion or along the base of the landfill (3)(2)(5) to remove and collect the leachate. Further treatment of the collected leachate would be required to reduce the pollutants to acceptable discharge levels, assuming that treatment technology is available. In any event, additional construction and operating costs would be required.

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We now propose a different approach to remove hazardous materials in the leachate within the landfill site and eliminate the need for additional treatment of the leachate. The approach is to line the landfill site with an impermeable membrane and to remove the leachate from the landfill and permitting it to percolate through a bed of inexpensive material whose sorbent and exchange characteristics are satisfactory for reducing the concentration of pollutants to acceptable discharge levels thereby preventing contamination of ground and surface waters.

A laboratory study was conducted in order to evaluate the effectiveness for contaminant removal of ten natural and synthetic sorbent materials on the leachate and liquid portion generated from three different industrial sludges. The sludges chosen for this study were a calcium fluoride sludge (of the type generated by the electronic and air-craft industries), a metal finishing sludge and a petroleum sludge. These sludges were selected because their annual production is of a significant magnitude to present disposal problems and the leachate from these sludges would contain a cross-section of hazardous and toxic organic constituents, heavy metal hydroxides, toxic anions such as cyanide and substantial amounts of fairly soluble toxic salts such as calcium fluoride. The sorbent materials used are fly ash, bottom ash, Ottowa sand, activated carbon, illite, kaolinite, vermiculite, natural zeolites, cullite and activated alumina (mesh size <325; 48-100 and <100). Container studies were conducted to evaluate the batch-wise "static" sorption and exchange capacity of the sorbent materials using maximum background concentrations of contaminants in the leachate. These batch studies are then followed by lysimeter studies in order to obtain information regarding the dynamic capacity and permeabilility characteristics of these materials. Leachate analysis involved the determination of pH, conductivity, residue, chemical oxygen demand (COD), total organic carbon (TOC), anionic species and cationic species before and after contact with sorbent materials.

EXPERIMENTAL

Preparation of Sorbent Materials

All sorbent materials were used as received. Sorbent materials which were not obtained as a powder (i.e., illite, bottom ash and vermiculite) were ground and passed through an 80-mesh A.S.T.M. standard sieve. All sorbents were dried to constant weight at 103°C (in accordance with "Standard Methods") and stored in a dessicator until used.

Preparation of Sorbent Leachate

Background mixtures of deionized water and dried sorbent material were prepared in the ratio of 2.5 ml water/gram of sorbent material and agitated in a Burrell Shaker for 24 hours at ambient temperature. Preliminary studies revealed that saturation of the mixture with respect to total dissolved solids was achieved in 24 hours. The resultant mixture was then filtered using a glass fiber filter (Reeve Angel type 934A) in order to remove all undissolved and non-filterable solids. The filtrates (leachates) were then stored in plastic screw cap bottles at ambient temperature until used.

Preparation of Sludge Leachates

A sample of each type of sludge was dried at 103°C to determine its moisture content. The unaltered sludge was then mixed with deionized water in a ratio of 2.5 ml water per gram of dried sludge (as determined by the above moisture content consideration) and mechanically stirred for 24 hours. The above ratio was selected after a series of trial ratios involving decreasing quantities of water in the mixture indicated that maximum sludge leachate concentrations were achieved. At the end of that time, the mixture was filtered through a glass fiber (Reeve Angel type 934A). The resultant filtrate was stored in a screw-capped plastic bottle at ambient temperature until used.

Batch Studies

Into a tared 1 liter screw-capped polypropylene Erlenmeyer flask was weighed 100 grams of dried sorbent materials. To this was added 250 ml of sludge leachate. The flask was sealed and agitated for 24 hours at ambient temperature. At the end of this time, the mixture was filtered through a glass fiber filter and the filtrate stored in sealed plastic flasks at ambient temperature until analyzed.

Dynamic Studies

In order to simulate dynamic conditions, lysimeter studies were conducted using 500 g of sorbent material, except for activated carbon where 250 g were used. The lysimeters were constructed of plexiglass tubing (5.8 cm i.d.; 0.6 cm wall thickness; 90 cm length). The sorbent material was packed into the lysimeter and supported by a porous corundum disc (6.5 cm diameter; 0.6 cm thickness). Leachate was permitted to flow through the sorbent material maintaining a constant hydraulic head. Samples were then collected at regular time intervals and analyzed for specific parameters.

Sources of Sorbent Materials

(1) Zeolite: This material is from the Buckhorn New Mexico Mine and was supplied by Double Eagle Petroleum and Mining Company, Casper, Wyoming.
(2) Cullite: (Hi-capacity Cullite, 16-40 mesh; white particles) supplied by Culligan USA, Culligan International Company, Northbrook, Illinois.
(3) Illite: Obtained from A.P. Green Refractory Company Morris Plant, Morris, Illinois.
(4) Kaolinite: Supplied by Georgia Kaolin Company, Elizabeth, New Jersey.
(5) Vermiculite: Obtained from W.R. Grace & Co., Trenton, New Jersey.
(6) Bottom Ash and Fly Ash: Supplied by Public Service Electric & Gas Company Hudson Generating Station, Jersey City, New Jersey.
(7) Activated Carbon: (Grade 718) Obtained from Witco Chemical, Activated Carbon Division, New York, New York.
(8) Activated Alumina: Supplied by Alcoa.

RESULTS AND DISCUSSION

Comprehensive analyses were performed in accordance with standard methods on leachates generated from two calcium fluoride sludges, two metal finishing sludges, and one petroleum sludge.

The parameters chosen for analysis for each specific sludge was determined on the basis on results obtained from emission spectroscopic and x-ray fluorescent analysis of the leachates. Analyses were initially performed for the following heavy metals: Copper, iron, nickel, lead, zinc, chromium and cadmium. Further analyses were performed for calcium and magnesium ions (which contribute to hardness in water) and fluoride, chloride and cyanide ions (which, if in high concentrations in raw water supplies, could cause rejection of same as a potential drinking water supply source).

The findings given in Tables I through V indicate only those ions where concentration levels are such that they could be measured by the use of atomic absorption and specific ion equipment. Tables I through V indicate the analyses of the leachates generated from the abovementioned sludges prior to their mixing with the ten respective sorbent materials. In addition, the analysis of the leachate generated with deionized water from each of the sorbent materials was also analyzed. Upon completion of the above, batch studies were performed (as described above) to develop the following data:

1 - The sorption capability of the respective sorbent materials tested for specific constituents (in micrograms per gram of sorbent used, or µg/g).
2 - The removal efficiency of the sorbent material studied for those ions in the respective sludges.

(a) Calcium Fluoride Sludges: The analysis of the calcium fluoride sludge leachates show signifigant concentrations of calcium, magnesium, copper, fluoride, chloride and cyanide ions (see Tables I and II). Also, signifigant levels of organics as represented by the COD, TOC measurements were observed.

In analyzing the results in terms of micrograms removed per gram of sorbent used it is interesting to note that those effective sorbent materials found for each specific ion studied tend to achieve approximately the same values of sorbent capacity. Thus, the removal capacities of effective sorbents are within a relatively close range.

Tables VI and VII show percent removals of various sorbents for the parameters studied. The following can be appreciated:

1 - There is no single sorbent material which is effective in removing all measured; however, all of the parameters with the exception of chlorides can be effectively removed by some sorbent material. As shown in Tables VI and VII, a combination of two or three sorbent materials can virtually remove all objectionable ions found in the calcium fluoride sludges.

2 - Regarding the specific ions in the sludge leachate, namely calcium, fluoride and cyanide: Of the naturally occurring sorbents, illite and zeolite were found to be the most effective for fluoride removed. Among the synthetic sorbents, activated alumina and cullite were best able to reduce fluoride levels. Illite (natural sorbent) and activated carbon (synthetic sorbent) were the only sorbents able to effectively reduce the leachate levels of cyanide ion. Calcium ion removal was dramatically accomplished by both of the synthetic sorbents, cullite and activated alumina. Regarding the natural sorbents, only zeolite achieved a significant amount of removal.

3 - It should be pointed out that although none of the sorbents were found to be effective in chloride ion removal from the calcium fluoride sludge leachate, the levels involved in the leachate, i.e., 78 mg/l and 59 mg/l, are well within acceptable levels set by the U. S. Public Health Service (250 mg/l) for drinking water supplies. Consequently, the chloride levels present no problem.

(b) Metal Finishing Sludges: The analyses of the metal finishing sludge leachates indicate potentially high concentrations of nickel, fluoride and chloride ions. In addition, the leachates were also analyzed for COD, TOC, calcium, and magnesium ions.

Tables III and IV record the sorbent capability of the various materials tested on the sludge leachate in terms of µg removed per gram of sorbent used. Regarding the removal efficiencies, the following were found (see Tables VIII and IX):

1 - As in the case of the calcium fluoride sludge leachates, there is no single sorbent material which is effective in removing all ions from the leachates examined. However, with the exception of chloride ion removal, there can be found a combination of two or three sorbents which may in combination effectively reduce all other ions studied.

2 - Regarding removal efficiencies, it was found that of the natural sorbents, only illite and kaolinite were effective in reducing fluoride leachate levels (see Tables VIII and IX). Of the synthetic materials, nickel ion removal was effectively achieved with activated alumina and activated carbon, both synthetics. To a lesser extent, the naturally occurring vermiculite and kaolinite were also effective. Considering chloride ion removal efficiency, only illite (natural) was found to be moderately successful in reducing chloride levels in the leachate. In both metal finishing sludges, the efficiencies achieved (36% and 39%) were sufficient to reduce chloride levels to acceptable raw water standard.

(c) Petroleum Sludge: The petroleum sludge exhibited high COD, TOC, calcium, magnesium, nickel, lead, fluoride, chloride and cyanide levels.

Table V lists the values of each parameter examined in terms of micrograms material removed per gram of sorbent used. Considering removal efficiencies of the abovementioned parameters (see Table X) the following was found:

1 - Of the synthetics, activated carbon was found to be the most successful in lowering both COD and TOC levels in the leachate. Illite was found to be the most successful of the natural sorbents.

2 - All of the synthetic sorbents were extremely effective in removing calcium

and magnesium ions. Moderate success was achieved for calcium by the use of the natural illite. None of the natural sorbents were able to appreciably reduce magnesium ion levels.

3 - Fluoride ion removal was successfully achieved with the use of illite (natural), kaolinite (natural), and activated carbon (synthetic). Activated alumina (synthetic) was effective as well, to a lesser extent.

4 - Cyanide ion removal was best achieved by activated carbon (synthetic) and to a lesser extent by illite (natural). However, only activated carbon treatment was effective in reducing cyanide leachate levels to a concentration acceptable for raw drinking water purposes.

5 - Nickel ion removal can moderately be achieved by using activated alumina as a sorbent material. None of the other sorbents achieved any reasonable success in sorbing nickel ions. Fortunately, the leachate nickel background in the petroleum sludge studied was sufficiently close to acceptable raw drinking water standards to require little treatment. If, however, such background values should increase markedly, further study would be required to achieve higher removal efficiencies by the sorbent or combinations of sorbents required.

6 - Lead ion reduction by all the sorbents was virtually non-existent. Further studies will be needed to solve this problem.

7 - Chloride levels present a problem. Although some removal can be achieved by all of the sorbents studied (with illite and activated carbon found to be the most effective), the high chloride background, namely 10,990 mg/1, is so large that percent removals in the high ninety percentiles would be required in order to achieve acceptable an acceptable level of chloride ion.

In summation, lead and chloride ion levels continue to present a problem as shown by the initial batch studies performed on the petroleum sludge.

WORK IN PROGRESS

The abovementioned batch studies represent a first-cut approach at a design for removing objectionable ions from sludge leachates. It is appreciated by the authors that the studies described above do not closely simulate anticipated field design conditions nor do they consider the application of various combination of sorbent materials. To this end, further studies are being conducted with the use of lysimeters in an attempt to more closely approximate the true conditions that sorbent materials would be subjected to when surcharged with sludge leachates. Preliminary results from these studies (as shown in Table XI) indicate much greater removal efficiencies with the same sorbent materials than was found in the batch studies. Breakthrough points are being simultaneously determined during the lysimeter studies. (Breakthrough point in these tests is considered to be the development of effluent concentrations, for each ion tested, which exceed acceptable raw water drinking levels.)

Preliminary results indicate that some of the sorbents tested are effective in retarding breakthrough.

SUMMARY AND CONCLUSIONS

(1) There are a number of sorbent materials (both natural and synthetic) which have been found effective in removing objectionable ions from industrial sludge leachates.

(2) Although no single sorbent material was found to be effective in removing all objectionable ions from the sludge leachates studied in general, two or three different sorbent materials could be collectively combined to reduce sludge leachate effluent levels to acceptable values.

(3) Preliminary lysimeter studies indicate that considerably higher removal efficiencies can be achieved than were achieved in the batch studies using the same sorbent materials. Considering the success indicated in the batch studies, the authors are convinced that the results of the lysimeter studies will provide some valuable design data for removing industrial sludge leachates in the field on a cost-effective basis.

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TABLE 1. BATCH STUDY RESULTS OF CALCIUM FLUORIDE (LOWER PIT) SLUDGE LEACHATE

Measured Parameters	Initial Condition of Leachate	Description	Bottom Ash	Fly Ash	Zeo-lite	Vermi-lite	Il-lite	Kaolite	Acti-vated Alumina (I)	Acti-vated Alumina (II)	Cullite	Activated Carbon	Acceptable Raw Water Standard
pH	4.3	Background of Sorbent Material	7.2	8.5	7.8	8.1	3.0	5.1	9.8	9.7	9.0	9.4	
		Amt. Remaining After Treatment	6.0	10.2	7.5	7.3	3.0	4.2	8.8	9.3	7.9	9.9	
Conductivity	3620	Background of Sorbent Material	2780	2500	8150	182	4460	295	2790	3030	4010	575	
		Amt. Remaining After Treatment	5200	2990	7000	2800	4490	1980	3390	3670	1860	2280	
Total Dissolved Solid(mg/l)	2783	Background of Sorbent Material(mg/l)	1853	2901	7224	136	3985	32	1254	1907	3296	426	
		Amt. Remaining After Treatment(mg/l)	4573	3188	9826	2925	4316	3439	2097	3603	5130	2924	500
		mg Removed per g of Sorbent Used											
Total Dissolved Volatile Solid (mg/l)	329	Background of Sorbent Material(mg/l)	526	582	530	30	900	112	332	555	391	10	
		Amt. Remaining After Treatment(mg/l)	490	467	809	422	908	644	304	505	465	260	NA
		mg Removed per g of Sorbent Used											
Total Dissolved Fixed Solid (mg/l)	2454	Background of Sorbent Material(mg/l)	1327	2319	6606	106	3085	202	922	1352	2905	416	
		Amt. Remaining After Treatment(mg/l)	4083	2721	9017	2503	3408	2795	2593	2710	4665	2664	NA
		mg Removed per g of Sorbent Used											
COD(mg/l)	76	Background of Sorbent Material(mg/l)	60	5	27	13	16	7	24	22	21	< 2	
		Amt. Remaining After Treatment(mg/l)	80	39	76	53	48	140	65	90	67	2	NA
		mg Removed per g of Sorbent Used	0	93	0	58	70	0	0	0	0	185	
TOC(mg/l)	16.5	Background of Sorbent Material(mg/l)	0.0	4.1	0	2.7	0.0	13.5	37.6	76.0	40.1	5.1	
		Amt. Remaining After Treatment(mg/l)	0.0	0.0	16.6	19.9	0.0	26.0	16.3	45.7	17.5	5.1	NA
		mg Removed per g of Sorbent Used	41.3	41.3	5.3	16.0	41.3	0.0	0.5	0.0	0.0	28.5	
Ca(mg/l)	450.0	Background of Sorbent Material(mg/l)	20.0	300.0	6.0	1.5	2.5	42.0	< 0.1	< 0.1	< 0.1	0.3	
		Amt. Remaining After Treatment(mg/l)	385.0	465.0	135.0	600.0	335.0	355.0	0.75	< 0.1	< 0.1	327.0	NA
		mg Removed per g of Sorbent Used	37.5	0.0	662.5	0.0	182.5	112.5	998.1	999.0	999.8	182.5	
Cu(mg/l)	0.22	Background of Sorbent Material(mg/l)	0.25	0.06	0.07	0.03	3.55	0.16	0.04	0.03	0.42	0.03	
		Amt. Remaining After Treatment(mg/l)	0.10	0.02	0.05	0.07	3.66	0.29	0.02	0.07	0.31	0.06	NA
		mg Removed per g of Sorbent Used	0.30	0.50	0.43	0.38	0.00	0.00	0.50	0.38	0.20	0.40	
Mg(mg/l)	11.0	Background of Sorbent Material(mg/l)	95.2	3.2	169.0	[illegible]	[illegible]	[illegible]	0.1	< 0.1	0.2	< 0.1	
		Amt. Remaining After Treatment(mg/l)	52.0	1.0	60.0	20.2	48.0	14.0	0.6	1.1	3.0	1.5	NA
		mg Removed per g of Sorbent Used	0.0	25.0	0.0	0.0	0.0	0.0	26.0	24.8	20.0	23.8	
Cl^- (mg/l)	59	Background of Sorbent Material(mg/l)	590	10	128	3	3	7	44	38	7	5	
		Amt. Remaining After Treatment(mg/l)	470	60	180	56	40	50	99	91	61	75	250
		mg Removed per g of Sorbent Used	0	0	0	8	48	23	0	0	0	0	
F^- (mg/l)	6.08	Background of Sorbent Material(mg/l)	0.31	.71	0.51	1.21	0.33	2.28	2.09	2.28	0.30	0.06	
		Amt. Remaining After Treatment(mg/l)	2.55	2.19	1.65	5.89	0.66	3.08	1.59	1.85	2.02	4.85	1.5
		mg Removed per g of Sorbent Used	8.83	9.73	11.08	0.48	13.60	7.50	11.23	10.50	10.15	3.08	
CN^- (mg/l)	0.60	Background of Sorbent Material(mg/l)	0.70	0.06	0.06	0.02	0.02	1.20	0.22	0.02	0.02	0.02	
		Amt. Remaining After Treatment(mg/l)	0.46	0.56	0.56	0.50	0.15	1.60	0.48	0.53	0.66	0.10	0.20
		mg Removed per g of Sorbent Used	0.30	0.10	0.38	0.25	1.13	0.00	0.30	0.18	0.00	1.25	

Table II. Batch Study Results of Calcium Fluoride (Upper Pit) Sludge Leachate

Measured Parameters	Initial Condition of Leachate	Description	Bottom Ash	Fly Ash	Zeolite	Vermiculite	Illite	Kaolinite	Activated Alumina (I)	Activated Alumina (II)	Cullite	Activated Carbon	Acceptable Raw Water Standard
pH	7.5	Background of Sorbent Material	7.2	8.5	7.8	8.1	5.0	5.1	8.8	9.7	9.0	9.4	
		Amt. Remaining After Treatment	7.1	8.9	7.6	7.3	5.2	5.2	8.7	8.6	8.0	8.5	
Conductivity	3080	Background of Sorbent Material	2780	2500	8150	182	4660	295	1790	3030	4010	575	
		Amt. Remaining After Treatment	5950	3410	11550	3200	6150	2680	6130	5050	5000	2510	
Total Dissolved Solid (mg/l)	3390	Background of Sorbent Material (mg/l)	1853	2901	7226	136	3785	57	1256	1907	3296	426	500
		Amt. Remaining After Treatment (mg/l)	4848	3262	10189	3326	6625	3321	3037	3631	3697	2875	
Total Dissolved Volatile Solid (mg/l)	537	Background of Sorbent Material (mg/l)	526	582	530	30	900	112	332	555	391	10	NA
		Amt. Remaining After Treatment (mg/l)	581	328	603	667	667	404	308	442	263	224	
Total Dissolved Fixed Solid (mg/l)	2853	Background of Sorbent Material (mg/l)	1327	2319	6686	106	3085	202	922	1352	2905	416	NA
		Amt. Remaining After Treatment (mg/l)	4267	2934	9586	2857	3758	2917	2731	3189	3454	2651	
COD (mg/l)	89	Background of Sorbent Material (mg/l)	60	5	27	13	16	7	26	22	21	<2	NA
		Amt. Remaining After Treatment (mg/l)	89	52	94	67	60	90	98	110	96	<2	
		µg Removed per g of Sorbent Used	0	93	0	55	123	0	0	0	0	210	
TOC (mg/l)	8.5	Background of Sorbent Material (mg/l)	0.0	6.1	0.0	2.7	0.0	15.5	37.6	76.0	60.1	5.1	NA
		Amt. Remaining After Treatment (mg/l)	0.0	0.0	8.3	8.0	0.0	10.5	8.3	60.7	10.8	5.1	
		µg Removed per g of Sorbent Used	21.3	21.3	0.5	1.3	21.3	0.0	0.5	0.0	0.0	8.5	
Ca (mg/l)	365.0	Background of Sorbent Material (mg/l)	20.9	300.0	6.0	1.5	2.5	62	<0.1	<0.1	<0.1	0.5	NA
		Amt. Remaining After Treatment (mg/l)	261.0	365.0	88.0	318.0	300.0	231	0.1	5.0	0.3	1.1	
		µg Removed per g of Sorbent Used	260.0	0.0	692.5	117.5	162.5	335.0	912.3	900.0	911.8	909.8	
Cu (mg/l)	0.49	Background of Sorbent Material (mg/l)	0.03	0.06	0.07	0.03	3.55	0.16	0.06	0.03	0.42	0.03	1.0
		Amt. Remaining After Treatment (mg/l)	0.20	0.16	0.20	0.29	3.75	0.60	0.21	0.21	0.42	0.08	
		µg Removed per g of Sorbent Used	0.73	0.83	0.73	0.50	0.00	0.00	0.70	0.65	0.18	1.03	
Mg (mg/l)	5.0	Background of Sorbent Material (mg/l)	93.2	3.2	169	4.7	70.0	4.9	0.1	<0.1	0.2	<0.1	—
		Amt. Remaining After Treatment (mg/l)	96.6	3.3	176	9.7	75.0	9.9	0.2	1.7	0.4	1.1	NA
		µg Removed per g of Sorbent Used	0.0	4.3	0.0	0.0	0.0	0.0	12.0	8.3	11.5	9.8	
F^- (mg/l)	5.89	Background of Sorbent Material (mg/l)	0.31	1.71	0.51	1.21	0.33	2.28	2.04	2.28	0.30	0.04	1.5
		Amt. Remaining After Treatment (mg/l)	2.49	2.28	2.09	5.38	0.91	3.50	1.25	1.65	1.94	4.85	
		µg Removed per g of Sorbent Used	8.50	9.03	9.30	1.28	12.50	3.98	11.60	10.60	9.88	2.50	
Cl^- (mg/l)	78	Background of Sorbent Material (mg/l)	500	10	126	3	3	7	46	38	7	5	250
		Amt. Remaining After Treatment (mg/l)	682	88	195	80	70	76	95	110	86	67	
		µg Removed per g of Sorbent Used	0	0	0	0	20	10	0	0	0	22.3	
CN^- (mg/l)	0.42	Background of Sorbent Material (mg/l)	0.07	0.35	0.06	0.03	0.07	1.20	0.17	0.20	0.03	0.02	0.20
		Amt. Remaining After Treatment (mg/l)	0.47	0.30	0.44	0.43	0.26	1.11	0.52	0.58	0.42	0.10	
		µg Removed per g of Sorbent Used	0.00	0.00	0.00	0.00	0.63	0.00	0.00	0.00	0.00	0.00	

Table III. Batch Study Results of Metal Finishing Vacuum Filter Sludge Leachate

Measured Parameters	Initial Condition of Leachate	Description	Bottom Ash	Fly Ash	Zeolite	Vermiculite	Illite	Kaolinite	Activated Alumina (I)	Activated Alumina (II)	Cullite	Activated Carbon	Acceptable Raw Water Standard
pH	8.9	Background of Sorbent Material	7.2	8.5	7.8	8.1	3.2	5.1	9.8	9.7	9.0	9.4	
		Amt. Remaining After Treatment	8.7	9.3	8.2	8.3	3.6	7.1	9.6	9.6	9.5	9.9	
Conductivity	2000	Background of Sorbent Material	2780	2500	8150	182	4460	295	1760	3030	6010	575	
		Amt. Remaining After Treatment	3750	2890	8750	1185	3720	1075	2290	2900	2100	1700	
Total Dissolved Solid (mg/l)	1824	Background of Sorbent Material (mg/l)	1853	2901	7224	136	3685	52	1256	1907	3296	426	
		Amt. Remaining After Treatment (mg/l)	2770	3724	8158	1189	4276	1231	1751	7540	4364	1418	500
		µg Removed per g of Sorbent Used											
Total Dissolved Volatile Solid (mg/l)	516	Background of Sorbent Material (mg/l)	526	582	538	30	900	132	332	555	391	16	
		Amt. Remaining After Treatment (mg/l)	416	377	658	206	668	428	427	884	896	245	NA
		µg Removed per g of Sorbent Used											
Total Dissolved Fixed Solid (mg/l)	1308	Background of Sorbent Material (mg/l)	1327	2319	6686	106	3085	202	922	1352	2905	416	
		Amt. Remaining After Treatment (mg/l)	2356	2897	7500	903	3608	803	1324	1656	3670	1173	NA
		µg Removed per g of Sorbent Used											
COD	97	Background of Sorbent Material (mg/l)	60	5	27	13	16	7	24	22	21	<2	
		Amt. Remaining After Treatment (mg/l)	97	58	109	77	58	122	132	133	138	<2	NA
		µg Removed per g of Sorbent Used	0	98	0	50	118	0	0	0	0	238	
TOC	39.9	Background of Sorbent Material (mg/l)	0.0	4.1	0.0	2.7	0.0	25.5	37.5	76.0	40.1	5.1	
		Amt. Remaining After Treatment (mg/l)	8.6	23.3	32.8	20.6	3.1	42.3	41.6	112.6	63.7	5.1	NA
		µg Removed per g of Sorbent Used	78.3	41.3	17.8	49.3	92.0	0.0	0.0	0.0	0.0	87.0	
Ca (mg/l)	6.5	Background of Sorbent Material (mg/l)	20.0	300.0	6.0	7.5	2.5	42.0	<0.1	<0.1	<0.1	5.1	
		Amt. Remaining After Treatment (mg/l)	22.0	295.0	10.0	7.1	2.8	42.0	0.17	<0.1	<0.1	1.7	NA
		µg Removed per g of Sorbent Used	0.0	0.0	0.0	0.0	9.8	0.0	15.8	16.0	16.0	12.0	
Mg (mg/l)	18.0	Background of Sorbent Material (mg/l)	93.2	3.2	169.0	4.7	70.0	4.9	0.1	0.1	0.2	0.5	
		Amt. Remaining After Treatment (mg/l)	42.0	17.0	53.0	20.0	69.8	2.0	0.2	0.1	0.8	2.9	NA
		µg Removed per g of Sorbent Used	0.0	2.5	0.0	0.0	0.0	40.0	44.5	44.8	43.0	37.8	
Ni (mg/l)	0.15	Background of Sorbent Material (mg/l)	<0.05	<0.05	<0.05	<0.05	0.65	<0.05	<0.05	<0.05	<0.05	<0.05	
		Amt. Remaining After Treatment (mg/l)	0.12	0.08	0.14	0.06	0.68	0.05	0.15	0.05	0.20	<0.05	NA
		µg Removed per g of Sorbent Used	0.08	0.18	0.00	0.18	0.00	0.25	0.00	0.25	0.00	0.25	
F^- (mg/l)	1.20	Background of Sorbent Material (mg/l)	0.31	1.71	0.51	1.21	0.13	2.26	2.26	1.31	0.30	0.04	
		Amt. Remaining After Treatment (mg/l)	1.44	1.44	1.75	1.81	0.34	0.36	1.96	1.29	0.63	0.97	1.5
		µg Removed per g of Sorbent Used	0.00	0.00	0.00	0.00	2.13	2.13	0.00	[illegible]	1.93	0.58	
Cl^-	125	**Background of Sorbent Material (mg/l)**	500	10	120	3	3	7	66	58	7	2	
		Amt. Remaining After Treatment (mg/l)	510	135	245	105	76	95	170	160	130	130	250
		µg Removed per g of Sorbent Used	0	0	0	50	123	75	0	0	0	0	

Table IV. Batch Study Results of Metal Finishing (Settling Tank) Sludge Leachate

Measured Parameters	Initial Condition of Leachate	Description	Bottom Ash	Fly Ash	Zeolite	Vermiculite	Illite	Kaolinite	Activated Alumina (I)	Activated Alumina (II)	Calcite	Activated Carbon	Acceptable Raw Water Standard
pH	8.8	Background of Sorbent Material	7.2	8.5	7.8	8.1	5.0	5.1	9.8	9.7	8.0	9.6	
		Amt. Remaining After Treatment	8.3	9.0	8.1	8.8	3.1	7.6	10.3	9.2	8.9	9.7	
Conductivity	1670	Background of Sorbent Material	2700	2500	8150	182	4460	295	1700	3030	4010	575	
		Amt. Remaining After Treatment	3900	3000	7500	1360	4700	1370	2300	2200	5050	1610	
Total Dissolved Solid (mg/l)	1835	Background of Sorbent Material (mg/l)	1853	2901	7224	136	3685	32	1254	1907	3296	426	500
		Amt. Remaining After Treatment (mg/l)	2871	3948	8311	1600	5164	1383		3067	6936	1698	
Total Dissolved Volatile Solid (mg/l)	673	Background of Sorbent Material (mg/l)	526	582	530	30	600	113	553	555	391	10	
		Amt. Remaining After Treatment (mg/l)	368	854	442	522	1369	317		851	950	253	NA
Total Dissolved Fixed Solid (mg/l)	1162	Background of Sorbent Material (mg/l)	1327	2319	6686	106	3085	303	812	1352	2905	416	
		Amt. Remaining After Treatment (mg/l)	2503	3076	7869	964	3795	1068		2216	9880	1265	NA
COD (mg/l)	402	Background of Sorbent Material (mg/l)	40	5	27	11	16	7	36	22	21	<2	
		Amt. Remaining After Treatment (mg/l)	324	350	127	189	114	214	480	410	342	<2	NA
		μg Removed per g of Sorbent Used	195	130	688	533	720	470	5	0	150	1000	
TOC (mg/l)	156.6	Background of Sorbent Material (mg/l)	0.0	6.1	0.0	2.7	0.6	15.5	37.6	76.0	60.1	5.1	
		Amt. Remaining After Treatment (mg/l)	136.7	160.1	53.2	151.3	10.9	99.9	185.0	210.0	178.8	5.1	NA
		μg Removed per g of Sorbent Used	49.8	10.8	250.3	13.3	366.3	261.8	0.0	0.0	0.0	163.3	
Ca (mg/l)	13.5	Background of Sorbent Material (mg/l)	20.0	300.0	8.0	1.5	2.46	61	<0.1	<0.1	<0.1	0.5	
		Amt. Remaining After Treatment (mg/l)	25.0	305.0	15.0	8.0	2.55	35	<0.1	<0.1	<0.1	2.8	NA
		μg Removed per g of Sorbent Used	0.0	0.0	0.0	13.8	0.0	0.0	33.5	33.5	33.5	27.3	
Mg (mg/l)	20.0	Background of Sorbent Material (mg/l)	93.2	3.2	169.0	4.7	70.0	4.8	<0.1	<0.1	0.2	0.1	
		Amt. Remaining After Treatment (mg/l)	68.0	4.0	96.0	15.0	51.0	3.0	0.1	0.1	0.6	7.0	NA
		μg Removed per g of Sorbent Used	0.0	40	0.0	12.3	0.0	47.3	49.8	49.8	48.0	32.3	
Si (mg/l)	0.12	Background of Sorbent Material (mg/l)	<0.05	<0.05	<0.05	<0.05	0.65	<0.05	<0.05	<0.05	<0.05	<0.05	
		Amt. Remaining After Treatment (mg/l)	0.15	0.10	0.16	0.08	0.88	0.08	0.06	0.05	0.17	<0.05	NA
		μg Removed per g of Sorbent Used	0.00	0.05	0.00	0.10	0.00	0.10	0.15	0.175	0.00	0.175	
F^- (mg/l)	1.44	Background of Sorbent Material (mg/l)	0.31	1.72	0.51	1.21	0.85	2.28	2.06	2.28	0.30	0.04	
		Amt. Remaining After Treatment (mg/l)	1.68	1.62	1.90	2.03	0.35	0.69	1.73	1.39	0.18	1.17	1.50
		μg Removed per g of Sorbent Used	0.00	0.00	0.00	0.00	2.73	1.38	0.00	0.13	1.63	0.8	
Cl^- (mg/l)	360	Background of Sorbent Material (mg/l)	500	10	126	3	1	1	66	58	1	2	
		Amt. Remaining After Treatment (mg/l)	700	375	425	360	230	345	400	390	370	177	250
		μg Removed per g of Sorbent Used	0	0	0	0	323	28	0	0	0	438	

Table V. Batch Study Results of Bottom Tank Petroleum Sludge Leachate

Measured Parameters	Initial Condition of Leachate	Description	Bottom Ash	Fly Ash	Zeolite	Vermiculite	Illite	Kaolinite	Activated Alumina (I)	Activated Alumina (II)	Cellite	Activated Carbon	Acceptable Raw Water Standard
pH	7.4	Background of Sorbent Material	7.2	8.5	7.8	8.1	3.6	5.1	9.8	9.7	9.3	9.4	
		Amt. Remaining After Treatment	8.3	9.1	8.1	8.4	3.2	7.6	9.4	9.1	9.2	9.6	
Conductivity	15000	Background of Sorbent Material	2780	2500	8150	182	4660	295	1790	3530	6010	575	
		Amt. Remaining After Treatment	14800	14200	19000	8400	14200	13600	13200	13900	16000	13300	
Total Dissolved Solid (mg/l)		Background of Sorbent Material (mg/l)	1853	2901	7224	136	3905	32	1254	1907	3296	426	500
		Amt. Remaining After Treatment (mg/l)	16935	15163	22730	15012	16150	14506	12214	12086	20609	15085	
Total Dissolved Volatile Solid (mg/l)		Background of Sorbent Material (mg/l)	526	582	530	30	800	112	332	555	391	10	
		Amt. Remaining After Treatment (mg/l)	2214	1571	2101	1429	244	1398	626	490	1175	1001	NA
Total Dissolved Fixed Solid (mg/l)		Background of Sorbent Material (mg/l)	1327	2319	6686	106	3085	202	922	1352	2905	416	
		Amt. Remaining After Treatment (mg/l)	14721	13592	20623	13583	13856	13110	11590	12366	19236	14006	NA
COD (mg/l)	1299	Background of Sorbent Material (mg/l)	40	5	27	13	26	7	26	22	21	<2	
		Amt. Remaining After Treatment (mg/l)	1049	1048	1019	1014	663	1113	1069	1144	1131	105	NA
		µg Removed per g of Sorbent Used	628	629	703	711	1629	463	575	388	420	2985	
TOC (mg/l)	488.0	Background of Sorbent Material (mg/l)	0.0	4.1	0.0	2.7	0.0	15.5	37.6	76.0	60.1	5.1	
		Amt. Remaining After Treatment (mg/l)	365.0	358.0	378.0	367.0	201.0	363.0	367.0	357.0	405.0	28.0	NA
		µg Removed per g of Sorbent Used	207.5	225.0	175.0	202.5	617.0	212.5	252.5	327.5	207.5	1055.0	
Ca (mg/l)	327.0	Background of Sorbent Material (mg/l)	20.0	300.0	6.0	1.5	3.5	62.0	<0.1	<0.1	<0.1	0.5	
		Amt. Remaining After Treatment (mg/l)	342.0	327.0	327.0	330.0	161.0	315.0	7.6	.7	21.0	36.0	NA
		µg Removed per g of Sorbent Used	0	0	0	0	415.0	30.0	811.5	815.0	765.0	727.5	
Mg (mg/l)	400.0	Background of Sorbent Material (mg/l)	93.2	3.2	169.0	6.7	70.0	4.9	<0.1	<0.1	0.2	<0.1	
		Amt. Remaining After Treatment (mg/l)	438.0	397.0	356.0	390.0	372.0	385.0	1.6	5.0	99.0	213.0	NA
		µg Removed per g of Sorbent Used	0.0	7.5	110.0	25.0	70.0	37.5	996.0	987.5	902.5	667.5	
Ni (mg/l)	0.23	Background of Sorbent Material (mg/l)	<0.05	<0.05	<0.05	<0.05	0.65	<0.05	<0.05	<0.05	<0.05	<0.05	
		Amt. Remaining After Treatment (mg/l)	0.24	0.19	0.24	0.21	0.79	0.25	0.13	0.13	0.22	0.17	NA
		µg Removed per g of Sorbent Used	0.00	0.10	0.00	0.05	0.00	0.00	0.50	0.50	0.03	0.15	
Pb (mg/l)	0.48	Background of Sorbent Material (mg/l)	<0.20	0.30	0.30	<0.20	0.33	<0.20	<0.20	<0.20	<0.20	<0.25	
		Amt. Remaining After Treatment (mg/l)	0.61	0.48	0.78	0.50	0.59	0.43	0.43	0.43	0.47	0.48	NA
		µg Removed per g of Sorbent Used	0.0	0.0	0.0	0.0	0.0	0.13	0.13	0.13	0.13	0.0	
Zn (mg/l)	.06	Background of Sorbent Material (mg/l)	0.01	0.01	0.03	<0.01	1.66	0.27	<0.01	<0.01	0.08	<0.01	
		Amt. Remaining After Treatment (mg/l)	0.03	0.03	0.06	0.03	1.50	0.20	0.02	0.02	0.04	0.02	5.0
		µg Removed per g of Sorbent Used	0.08	0.08	0.05	0.05	0.00	0.00	0.10	0.10	0.05	0.10	
F^- (mg/l)	1.48	Background of Sorbent Material (mg/l)	0.31	1.71	0.51	1.21	0.33	2.78	2.09	2.28	0.50	0.06	
		Amt. Remaining After Treatment (mg/l)	0.89	1.26	1.00	1.43	0.22	0.17	0.44	0.49	0.86	0.17	1.5
		µg Removed per g of Sorbent Used	1.48	0.55	1.20	0.13	3.13	3.28	2.60	2.49	1.55	3.28	
Cl^- (mg/l)	10990	Background of Sorbent Material (mg/l)	500	10	126	3	3	7	44	38	7	5	250
		Amt. Remaining After Treatment (mg/l)	6736	6206	6136	6027	5084	6077	6382	4963	5495	2801	
		µg Removed per g of Sorbent Used	10635	11965	10635	12408	19675	17283	11520	15068	13738	20473	
CN^- (mg/l)	7.93	**Background of Sorbent Material (mg/l)**	0.07	0.06	0.06	0.02	0.02	1.20	0.22	0.20	0.02	0.02	
		Amt. Remaining After Treatment (mg/l)	2.96	4.96	2.99	3.38	1.38	5.33	5.33	7.15	7.15	0.30	0.20
		µg Removed per g of Sorbent Used	12.48	7.48	12.35	11.38	16.38	6.30	6.30	1.95	1.95	19.08	

Table VI. Percentage of Removal - Calcium Fluoride Sludge (Lower Pit) Leachate

Measured Parameters	Sorbent Materials									
	Bottom Ash	Fly Ash	Zeolite	Vermiculite	Illite	Kaolinite	Activated Alumina (I)	Activated Alumina (II)	Cullite	Activated Carbon
	Percentage of Removal									
COD	0	49	0	30	37	0	0	0	0	185
TOC	100	100	13	34	100	0	1	0	0	69
Ca	4	0	66	0	16	11	100	100	100	18
Cu	55	91	77	68	0	0	91	68	0	73
Mg	0	91	0	0	0	0	95	90	73	86
F^-	58	64	73	3	90	49	74	70	67	20
Cl^-	0	0	0	14	32	15	0	0	0	0
CN^-	20	7	10	17	75	0	20	12	0	83

Table VII. Percentage of Removal - Calcium Fluoride Sludge (Upper Pit) Leachate

Measured Parameters	Sorbent Materials									
	Bottom Ash	Fly Ash	Zeolite	Vermiculite	Illite	Kaolinite	Activated Alumina (I)	Activated Alumina (II)	Cullite	Activated Carbon
	Percentage of Removal									
COD	0	42	0	25	55	0	0	0	0	98
TOC	100	100	2	6	100	0	2	0	0	40
Ca	29	0	76	13	18	37	100	99	100	100
Cu	59	67	59	41	0	0	57	53	14	84
Mg	0	34	0	0	0	0	96	66	92	78
F^-	58	61	65	9	85	40	79	72	67	18
Cl^-	0	0	0	0	10	5	0	0	0	14
CN^-	0	0	0	0	62	0	0	0	0	76

Table VIII. Percentage of Removal of Metal Finishing (Vacuum Filter) Sludge Leachate

Measured Parameters	Sorbent Materials									
	Bottom Ash	Fly Ash	Zeolite	Vermiculite	Illite	Kaolinite	Activated Alumina (I)	Activated Alumina (II)	Cullite	Activated Carbon
	Percentage of Removal									
COD	0	40	0	21	49	0	0	0	0	93
TOC	79	42	18	48	92	0	0	0	0	87
Ca	0	0	0	0	60	0	97	99	100	74
Mg	0	6	0	0	0	89	99	99	96	84
Ni	20	47	0	47	0	67	50	67	0	67
F^-	0	0	0	0	72	72	0	0	64	19
Cl^-	0	0	0	16	39	24	0	0	0	0

Table IX. Percentage of Removal of Metal Finishing (Settling Tank) Sludge Leachate

Measured Parameters	Sorbent Materials									
	Bottom Ash	Fly Ash	Zeolite	Vermiculite	Illite	Kaolinite	Activated Alumina (I)	Activated Alumina (II)	Cullite	Activated Carbon
	Percentage of Removal									
COD	19	13	68	53	72	47	0	0	15	100
TOC	13	5	66	3	88	62	0	0	0	97
Ca	0	0	0	41	0	0	99	99	99	81
Mg	0	80	0	25	0	85	100	100	96	65
Ni	0	17	0	33	0	33	50	58	0	58
F^-	0	0	0	0	76	66	0	4	74	22
Cl^-	0	0	0	0	36	4	0	0	0	51

Table X. Percentage of Removal - Tank Bottom Petroleum Sludge Leachate

Measured Parameters	Sorbent Material									
	Bottom Ash	Fly Ash	Zeolite	Vermiculite	Illite	Kaolinite	Activated Alumina (I)	Activated Alumina (II)	Cullite	Activated Carbon
	Percentage of Removal									
COD	19	19	22	22	50	14	18	12	13	92
TOC	25	27	23	25	59	26	29	19	17	95
Ca	0	0	0	0	51	4	99	100	94	89
Mg	0	1	11	3	7	4	100	99	90	91
Ni	0	17	0	9	0	0	44	44	4	26
Pb	0	0	0	0	0	10	10	10	10	0
Zn	50	50	33	50	0	0	67	67	33	67
F^-	40	15	32	4	85	89	70	67	42	89
Cl^-	39	44	39	45	72	63	42	55	50	75
CN^-	63	38	63	57	83	33	33	10	10	96

Table XI. Comparisons of Removal Capacities of Fly ash in Batch and Lysimeter Tests (Calcium Fluoride Sludge Leachate)

	Batch Tests		Lysimeter Tests	
	Fly Ash (Acidic)	Fly Ash (Alkaline)	Fly Ash (Acidic)	Fly Ash (Alkaline)
F^- **	.0103	.0093	0.09	>0.05*
Ca	0.0000	0.0000	0.35	0.00
Cu	0.0000	0.0002	> 0.0014*	>0.0003*
Mg	0.0000	0.0413	0.025	>0.105*

* Removal still in progress

** Capacities are expressed in mg of ion removal per g of sorbent used

PROBLEMS ASSOCIATED WITH THE LAND DISPOSAL OF AN ORGANIC INDUSTRIAL HAZARDOUS WASTE CONTAINING HCB

by

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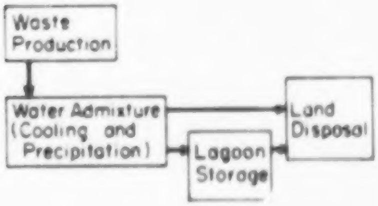
ABSTRACT

Hexachlorobenzene (HCB) is a persistent, water-insoluble, fat-soluble organic compound present in some industrial wastes. Its transport in moving water would be negligible but its long term persistence allows significant volatilization to occur. Adequate coverings are desired to reduce or eliminate HCB vapor movement when the wastes are applied to land. Research was initiated to determine under what conditions, if any, it is safe to dispose of HCB-containing waste on land. The volatilization fluxes of hexachlorobenzene from industrial wastes were determined using coverings of soil, water and polyethylene film in a simulated landfill under controlled laboratory conditions. Coverings of water and soil were found to be highly efficient in reducing volatilization. Polyethylene film was less efficient when compared on a cost basis. Volatilization flux through a soil cover was directly related to soil air-filled porosity and was therefore greatly reduced by increased soil compaction and increased soil water content. An organic liquid phase associated with the hex waste was heavier than water and contained 1.4% HCB by weight. The presence of HCB in this liquid phase creates the potential for the rapid transport of HCB in porous media.

Land disposal of industrial wastes containing hexachlorobenzene (HCB) has been practiced for a number of years in the United States and elsewhere. A recent episode of HCB contamination of beef cattle from farms in the vicinity of a municipal landfill receiving HCB-containing industrial wastes has caused concern for and a reevaluation of present procedures in operation at such landfills.

Hexachlorobenzene is present in industrial waste as a by-product in the commercial production of several chlorinated solvents such as perchloroethylene and carbontetrachloride (7). HCB is a registered fungicide used as a seed protection chemical for seed grains. In addition significant quantities of HCB are produced as impurities or by-products in the production of certain pesticides such as PCNP, dacthal, mirex, simazine, atrazine, and propazine. Industry has used several methods to dispose of the large quantities of hexachlorobenzene-containing waste (hex waste). These methods include municipal landfill, land burial, lagooning, deep well injection, incineration, and product recovery. Land disposal in municipal landfills and land burial will be the topic of this paper. Land burial is distinguished from municipal landfill in that land burial is a procedure used by the waste manufacturer on his own property. Lagooning is a method whereby hex waste is temporarily stored under water in an unlined reservoir prior to being placed into a landfill. Hence, this project includes the effectiveness of a water cover in reducing volatilization.

A typical operation where land disposal of hex waste is used is as follows:



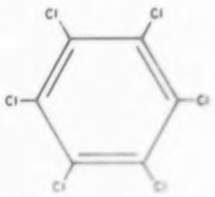
The solid phase remaining after the water admixture step may be either hauled directly to the final land disposal site or temporarily remain in a lagoon storage site. In cases where lagoon storage is used, the cooling and crystallization step (water admixture) and lagooning are one and the same. That is, the waste stream from the production process is fed directly below the water surface of a water lagoon. Cooling and precipitation take place and the solid phase stored under water in the lagoon. Periodically, the lagoon is emptied and the hex waste carried by truck to the land disposal site.

This study was initiated because of a specific instance of HCB contamination of beef cattle in December, 1972 in southern Louisiana. Beef cattle to be slaughtered for consumption were quarantined from sale in a 200-square mile area because of high levels of HCB in their fat tissue. Following extensive investigations by local, state and federal agencies and the cooperation of HCB-producing industries in the area, the source of the HCB was traced to the disposal of waste containing HCB in a municipal landfill. Uncovered trucks had been used to haul hex waste from the industrial source to the landfill. This led to spillage and contamination along the pathways followed by the trucks. Waste material deposited at the landfill sites was left uncovered. It was reported that the hex waste was being used as a covering over municipal waste as a fly-repellent. Disposal of hex waste in municipal landfills has ceased in affected areas in southern Louisiana. The uncovered waste at these landfills has been collected into a small area of the landfill and covered with 4 to 6 feet of soil, with a 10-mil thick sheet of polyethyelene film buried approximately midway in the soil cover.

The disposal of hex waste in landfill sites in southern Louisiana has resulted in a pattern of HCB contamination of residents in the area, operators of the municipal landfills, beef cattle, and soil, plant and air samples (1, 6, 11, 12). Soil and plant samples taken from near landfill areas used for disposal of hex waste showed decreasing HCB contents as distance from the landfill increased (6).

Burns and Miller (1) reported high levels of HCB in the plasma of individuals exposed through the transportation and disposal of hex waste in southern Louisiana. In a sampling of 29 households situated along the route of trucks containing hex waste, the average plasma level of HCB was 3.6 ppb with a high of 23 ppb. The range for landfill workers was 2 to 345 ppb plasma HCB. The average plasma HCB level in a control group was 0.5 ppb with a high of 1.8 ppb.

Hexacholorbenzene is a stable persistent compound of low water solubility and moderate vapor pressure. It exists as a white powder at room temperature. Its empirical formula is C_6Cl_6 and its structural formula is:



Hexachlorobenzene (HCB)

HCB has a melting point of 230°C and sublimes at 322°C (4). Little information is available in the literature on HCB solubility, but it is essentially insoluble in water. We have measured its solubility in water to be 6.2 μg/l. Sears and Hopke (7) reported a vapor pressure of 2.10 x 10^{-5} mm Hg at 25°C for HCB. We have measured its vapor pressure to be 1.91 x 10^{-5} mm Hg at 25°C. HCB is soluble in several organic solvents such as benzene and hexane and is soluble in fats and oil. Hence it tends to accumulate in the fatty tissues of animals. HCB should not be confused with the organochlorine insecticide lindane which is hexachlorocyclohexane ($C_6H_6Cl_6$) even though it has the common name BHC for benzene hexachloride.

Based on the pattern of HCB contamination of soils and plants in the Louisiana incident, its moderate vapor pressure, low water solubility, and long-term persistence, it was concluded that volatilization and subsequent transport by moving air currents would be the principle mechanism by which HCB would move about the environment. Presently there has been no information to indicate that significant degradation of HCB occurs in the environment. This means that HCB persists long enough that even with its moderate vapor pressure, significant quantities can escape into the atmosphere and can be redistributed by moving air currents.

Therefore, research was initiated on the volatilization of HCB from hex waste disposed of on land. Similar disposal problems could be expected with any waste material containing organic compounds of moderate vapor pressure and persistence deposited on land and the results of this investigation would be expected to apply to these compounds as well. The objective of this study was to determine the conditions, if any, under which it is safe to dispose of HCB on land. The effectiveness of various coverings - soil, water, polyethylene film - in reducing HCB volatilization from land was specifically investigated. In pursuing this objective it was assumed that vapor phase movement to the soil surface and subsequent volatilization from the soil surface is the only pathway by which HCB moves. For detailed discussions of factors affecting the volatilization of organic compounds from soils and on vapor phase movement in soils the reader is referred to recent review articles by Spencer, Farmer, and Cliath (10) and Letey and Farmer (5).

SIMULATED LANDFILL

In order to determine the effectiveness of various coverings on the volatilization of HCB from industrial waste, the simulated landfill apparatus as depicted in Figure 1 was constructed and operated under laboratory conditions so that critical factors such as temperature and air flow rate could be closely controlled and monitored.

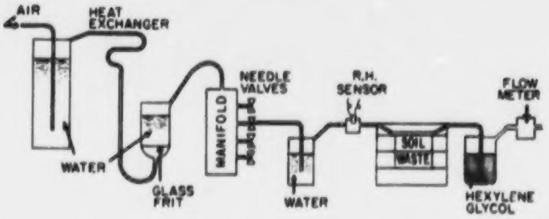


Figure 1. Closed air flow system for collecting volatilized HCB from simulated landfill.

The soil used for the volatilization experiments had been collected from a municipal landfill in Louisiana where industrial hazardous waste containing HCB had been previously deposited. The soil was a silty clay loam with an organic matter content of 1.4% and a field bulk density of 1.2 g/cm^3. Samples of hex waste to be used in the simulated landfill apparatus were collected directly from two separate manufacturers of chlorinated solvents. Hex waste samples A and B, as collected from the manufacturer, contained 54.9% and 56.9% HCB, respectively. The samples were air-dried at room temperature before being used in the simulated landfill. After air drying the HCB contents of samples A and B increased to 65.7% and 90.5% HCB, respectively. A third material used in the volatilization experiment was recrystallized practical grade HCB which was 98+% hexachlorobenzene. We found no differences in the volatilization of HCB from these materials in the simulated landfill. That is, HCB volatilized from all the materials as if they were pure HCB. (There was one exception to this which occurred with the use of the waste without air drying. In this case the presence of a reddish-brown liquid in the samples caused more rapid HCB loss as will be discussed later.)

The volatilization cell consisted of plexiglass sections bolted together with O-ring seals between the sections. Hex waste was placed in the bottom section and soil or other coverings placed in the section above the hex waste. The cover or top section of the volatilization cell contained a cavity 2 mm deep which allowed air flow over the surface of the covered hex waste. An air flow rate of 0.769 l/minute was used in this study which provided an air speed across the soil surface of 21.5 cm/sec (0.48 mile/hr). The apparatus utilized a closed air flow system with the volatilized HCB collected in hexylene glycol traps in a manner similar to that used by Farmer et al. (3) to measure the volatilization of insecticides from soils. The entire simulated landfill operation was carried out inside a temperature-controlled cabinet maintained at 25°C. Volatilization processes are extremely dependent on temperature due to the temperature dependence of vapor pressure. The hexylene glycol traps were changed at suitable intervals and the trapped HCB extracted into hexane to be analyzed by gas liquid chromatography using an electron capture detector. Prior to analysis by GC most of the samples obtained from the industrial waste required a column cleanup on activated neutral alumina to remove a great number of interfering compounds which are present in the industrial waste samples.

Sample Cleanup

Considerable difficulty was encountered with the GC analysis of several of the volatilized samples from the industrial waste. Tailing solvent peaks, unstable base lines, overlapping peaks, and dirty detectors were common occurrences. The difficulties were assumed to be caused by the presence in the hex waste of interfering compounds which volatilized into the air in the simulated landfill and were extracted into the hexane along with HCB. Certainly, one would suspect the formation of compounds with similar chemical and physical properties to those of HCB during the industrial manufacturing process. A column cleanup procedure was developed using activated neutral alumina to remove the interferences. Anhydrous sodium sulfate was layered on top of the alumina to remove any traces of water which may have been present in the hexane extract containing the HCB. The hexane sample was first placed on the cleanup column. The column was then eluted with pure hexane followed by 10% benzene in hexane. Essentially all of the HCB minus the interfering compounds eluted with the 10% benzene in hexane fraction. This cleanup procedure was considered to be a significant development. Essentially no information exists in the literature on procedures suitable for the cleanup of industrial waste samples for analysis by GC.

RESEARCH FINDINGS

The factors investigated for their effect on HCB volatilization included soil compaction, soil water content, soil depth, temperature, use of a polyethylene film barrier, source of waste, and a water cover. HCB volatilization through these coverings were compared with HCB flux from uncovered wastes. The flux from uncovered hex waste in the simulated landfill apparatus at 25°C and 0.769 ml/min air flow rate was 8700 ng/cm^2/day.

Soil Compaction and HCB Volatilization

When in a field situation and faced with a decision of what to do to a landfill site to reduce volatilization of an organic compound from a buried waste, one has a limited number of choices available. One of these choices is whether or not to go to the expense of compacting the soil cover in the landfill. Soil cover is used to reduce the volatilization of HCB. Since HCB is almost insoluble in water, diffusion in the vapor phase will be the major mode of movement through soil. Soil compaction or soil bulk density determines the porosity of a soil and thus affects HCB vapor flux. Data presented in Figure 2 show that HCB fluxes from cover soil with a bulk density of 0.96 g/cm^3 (low compaction) are greater than those from cover soil with a bulk density of 1.15 g/cm^3 (high compaction).

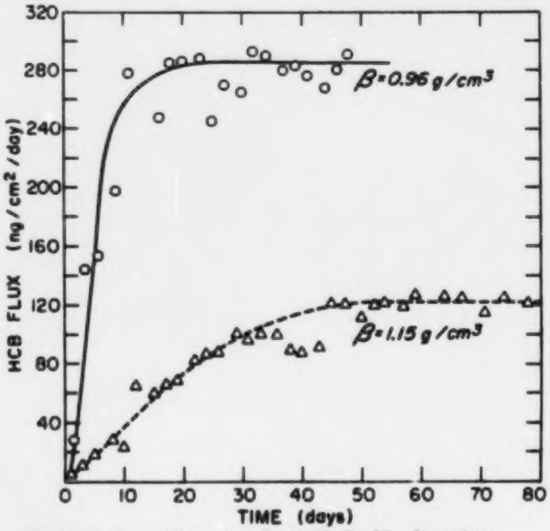


Figure 2. Effect of soil bulk density on the volatilization of HCB from industrial hazardous waste covered with 1.9 cm (3/4 in.) soil.

The final soil water contents were very close for these two experiments and the major effect can be attributed to the effect of bulk density on air-filled porosity. Calculation of the effect of air-filled porosity on steady state diffusion shows that increasing relative air-filled porosity by 34% increases HCB flux by more than a factor of two. Similar exponential effects of air-filled porosity on vapor phase diffusion flux has been shown for lindane (2).

Thickness of Soil Cover and HCB Volatilization

Thickness of soil cover affects the distance an HCB molecule has to travel. The distance or pathlength determines the concentration gradient which is the driving force for diffusion. Thus the flux is also affected by the soil thickness. Figure 3 shows that HCB flux from hex waste covered with 1.9 cm (3/4 inch) of soil is greater than that covered with 2.5 cm (1 inch) of soil. HCB flux from 1.9 cm of soil cover reaches steady state at about 55 days. The flux from 2.5 cm of soil cover is still increasing at 55 days. HCB flux from the thicker soil cover will take a longer time to reach steady state and the final steady state HCB flux will be smaller because of the smaller concentration gradient. Covering hex waste with only 1.9 cm of soil reduces HCB flux from 8700 to 120 ng/cm^2/day or by 98.6% indicating that soil is a very effective covering material.

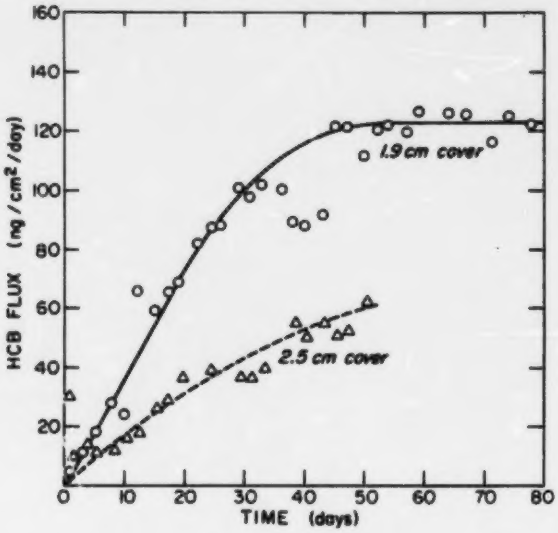


Figure 3. Effect of thickness of soil cover on HCB volatilization from industrial waste. Soil bulk density was 1.15 g/cm^3.

Soil Water Content and HCB Volatilization

To obtain maximum compaction of the cover soil, it is often necessary to add water to the soil while the soil is being compacted. Natural rainfall also adds water to the soil. The amount of water in a soil affects the air-filled porosity, or the pore space available for HCB vapor diffusion, and thus affects the HCB flux. Figure 4 shows the effect of soil water content on HCB flux. It is clear that HCB flux from 1.9 cm cover soil with a water content of 16.7% is greater than that from cover soil of 23.5% water content. Calculation of air-filled porosity shows that decreasing soil water content by 6.8% (dry weight basis) increases relative air-filled porosity by 27%, but because of the exponential effect of air-filled porosity on vapor diffusion, the HCB flux increases almost two times. From previous considerations of the effect of soil compaction, it is obvious that lower soil water content will have effects similar to that of lower soil compaction. The lower the soil water content of the cover soil, the more rapidly will the HCB flux reach steady state.

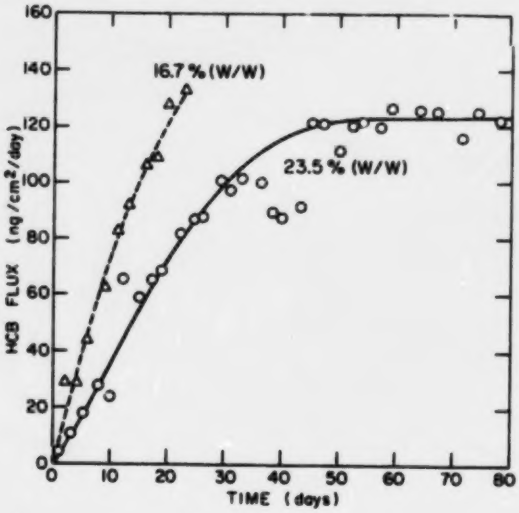


Figure 4. Effect of soil water content on HCB volatilization from industrial waste covered with 1.9 cm (3/4 inch) soil at bulk density of 1.19 g/cm^3.

Shearer et al. (9) studied lindane diffusion in soil and observed a similar exponential effect of soil water content on vapor phase diffusion. Increasing soil water content will decrease HCB volatilization flux. When soil is saturated with water it will have the same effect as a covering of water. A water cover was found to be very effective in preventing HCB volatilization. Covering the hex waste with 9/16 inch of water in the simulated landfill apparatus reduces the flux 1000 times.

Polyethylene Film in a Soil Cover and HCB Volatilization

Polyethylene film has been used together with soil in a municipal landfill as a cover for hex waste to reduce or prevent HCB volatilization. As will be shown later, polyethylene film is not very effective in preventing HCB volatilization when in direct contact with hex waste; however, its effectiveness may differ when used between soil layers. Figure 5 shows the effect of polyethylene film on HCB volatilization flux from hex waste covered with 1.9 cm of soil. Four-mil polyethylene film was sandwiched between two 0.95 cm soil layers. It is clear that the film reduces HCB flux and increases the time to reach maximum flux. However, the amount of reduction is not very large indicating that the film is not very effective as a barrier to HCB volatilization.

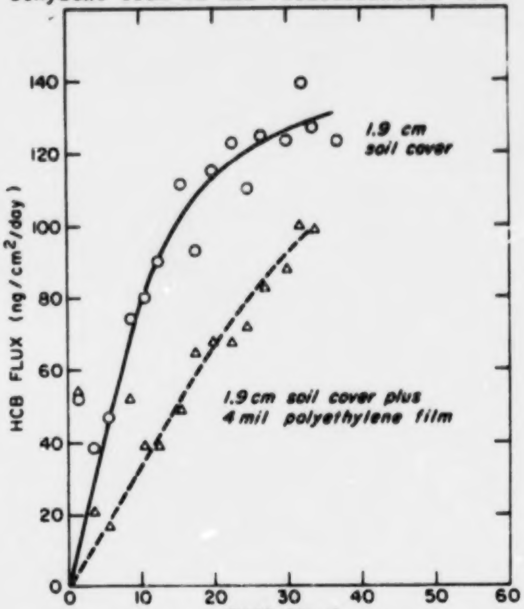


Figure 5. Effect of a composite soil plus polyethylene film cover on HCB volatilization from industrial waste.

Hex Waste Origin and HCB Volatilization

HCB volatilization from hex waste taken from two different industrial sources was studied to determine if different sources of hex waste would have significantly different HCB volatilization rates. Figure 6 shows HCB fluxes from two hex wastes covered with 1.9 cm soil. It is obvious that there is little difference in HCB volatilization from these two wastes. Both hex wastes gave a steady state flux of 123 ng/cm^2/day. Experiments with practical grade HCB also gave the same steady state HCB flux. Thus the vapor pressure of HCB in these two hex wastes must be similar to that in practical grade HCB.

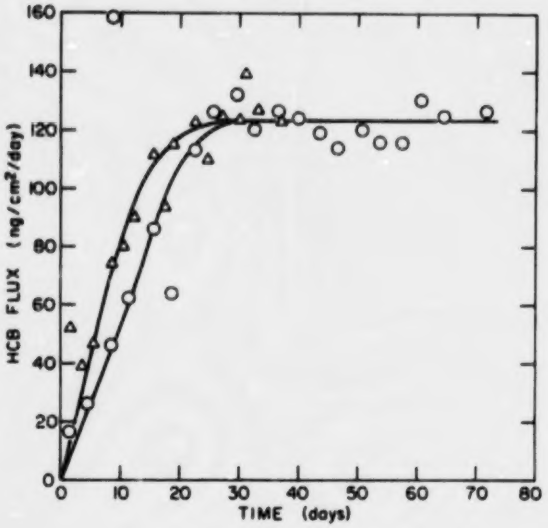


Figure 6. Volatilization of HCB from soil-covered industrial waste collected from two different manufacturers of chlorinated solvents.

Temperature and HCB Volatilization

HCB saturation vapor densities from practical grade HCB and hex waste at 15, 25, 35, and 45°C are shown in Table 1.

Table 1.
HCB saturation vapor densities from practical grade HCB and hex waste at 15, 25, 35, and 45°C.

Temperature °C	HCB µg/l	Hex waste µg/l
15	0.0630	0.0686
25	0.294	0.286
35	0.95	0.92
45	3.007	3.095

The vapor density of HCB at 25°C is equivalent to a vapor pressure of 1.91 x 10^{-5} mm Hg. The vapor densities from practical grade HCB and from hex waste are essentially the same. Increasing the temperature 10°C increases the vapor density about three and one-half times.

Vapor diffusion rate is dependent upon vapor density gradient and the diffusion coefficient. Both vapor density and diffusion coefficient increase with increased temperature. Changes in vapor density are considerably greater than changes in diffusion coefficient as temperature changes. Since HCB moves through soil by vapor diffusion, it is reasonable to expect that temperature effects on HCB volatilization flux will be about the same but somewhat greater than that on vapor density.

Assuming similar experimental designs, increasing temperature 10°C will increase HCB flux about three and one-half times. Thus, the effect of temperature on HCB volatilization flux is exponential. Ehlers et al. (2) studied lindane diffusion in soils and found that a similar exponential relationship existed between temperature and the amount of lindane diffused.

Effectiveness of Polyethylene Film for Reducing HCB Volatilization

Synthetic membranes are widely used as barriers to liquid and gas in the landfill operation. The effectiveness of one of these membranes, polyethylene film, as a barrier to HCB volatilization was tested in the laboratory without a soil cover. The polyethylene film was used alone without soil and was placed next to the waste. Figure 7 shows HCB fluxes from uncovered hex waste and from wet (solvated) and air-dried hex waste covered with 6 mil polyethylene film. Polyethylene film reduces HCB fluxes by 19% and 37% from wet and air-dried hex waste, respectively. The film does not seem to be very effective as a barrier to HCB volatilization. This supports the conclusion obtained in the section on a composite soil and film cover that the addition of polyethylene film to a soil cover was not very effective in reducing HCB volatilization compared to a soil cover alone.

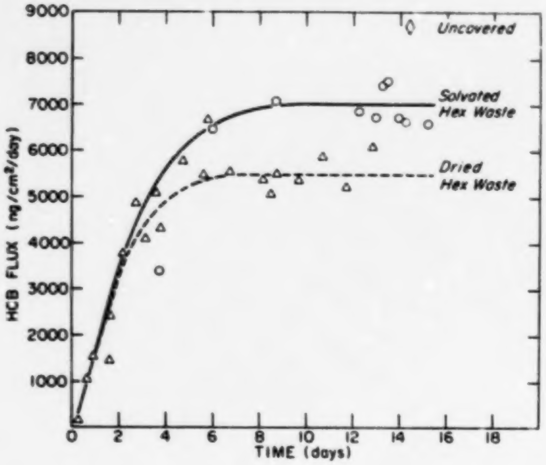


Figure 7. Effect of liquid phase in hex waste on volatilization of HCB from hex waste covered with polyethylene film. Volatilization from uncovered hex wastes is shown for comparison.

Problems Associated with Liquid Components of Waste

As mentioned earlier, the wet hex waste contained an amount of reddish-brown organic liquid. One waste sample from the solvent production process was found to contain as much as 76.6% liquid by volume. This particular sample had been collected prior to the water admixture step. The samples used in this study were collected after the addition of water to the waste stream and they contained only a small amount of the reddish-brown liquid. For most of the studies reported here the hex waste samples were air-dried to remove the organic liquid before the initiation of the experiments. For the data in Figure 7, the wet (solvated) hex waste sample was filtered only and therefore contained some reddish-brown organic liquid. This liquid portion of the waste was observed to deposit on the polyethylene film and to cause the film to partially dissolve and expand. The liquid waste may thus affect the HCB transmission property of the film. Figure 7 shows that HCB fluxes from wet hex waste covered with 6 mil film are greater than HCB fluxes from air-dried hex waste covered with the same film. Evidently, the liquid waste caused the film to expand and resulted in an increased HCB flux of about 28%. Since the reddish-brown liquid waste affects the polyethylene film causing it to partially expand, conceivably this liquid waste may also have deleterious affects on other synthetic membranes and thereby reduce their effectiveness as barriers to liquid and gas movement when used as such in a landfill.

The liquid portions of the waste was found to contain 1.4% HCB and have a density of about 1.67 g/ml. Because it is heavier than water, it may move downward when placed in a landfill and have a potential to leach HCB into ground water.

SUMMARY

The following comparison of HCB volatilization fluxes in kg/ha/yr of HCB illustrates the effectiveness of various coverings in reducing HCB losses from industrial wastes.

Uncovered Waste	317 kg/ha/yr
Covered	
Polyethylene film, 0.15 mm	201
Soil, 1.9 cm	4.56
Water, 1.43 cm	0.38
Soil (calculated), 120 cm	0.066

The above results are for soil collected from the landfill site and packed to a bulk density of 1.19 g/cm^3 with a water content of 17% by weight. The volatilization flux through the 120 cm of soil was calculated assuming diffusion in the vapor phase as the mechanism of movement. All other values were measured.

The effectiveness of the materials is water > soil > polyethylene film. (Polyethylene film is approximately as effective as water in reducing HCB flux when compared on an equal layer thickness. The cost of polyethylene film, however, precludes its use in thick layers.) Increasing soil bulk density and/or water content decreases HCB flux through soil. Increasing the layer thickness of all materials decreases HCB flux proportionally to the increase in thickness.

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A PRELIMINARY EXAMINATION OF VINYL CHLORIDE EMISSIONS FROM POLYMERIZATION SLUDGES, DURING HANDLING AND LAND DISPOSAL

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ABSTRACT

Vinyl chloride monomer (VCM) is retained in sludge wastes produced during polyvinyl chloride (PVC) processing at production plants. Industry is actively investigating processing improvements that may reduce the amount of VCM in these sludges in the future and is looking at alternate disposal and recycle schemes. However, the PVC sludges currently being disposed of at landfills may still contain sufficient VCM to constitute a potential health hazard when the gaseous VCM escapes. In a preliminary, low-level study done to determine whether a potential threat to the health of landfill workers or nearby residents exists, 17 grab air samples were collected for laboratory analysis of VCM content at three landfills where these sludges were disposed. Samples of the PVC sludges which were disposed at the three landfills also were collected. VCM concentrations in the grab air and sludge samples were measured using the gas chromatographic-flame ionization detection analytical technique. The release rate of VCM from sludge also was measured under controlled laboratory conditions, using a specially designed apparatus. The VCM emissions potential of the total sludge quantities disposed at these landfills was calculated.

INTRODUCTION

Early in 1974 it became apparent that there was a real need to establish the level of exposure to VCM of workers in the vinyl chloride/polyvinyl chloride (VCM/PVC) industry. This need was triggered by reports in January, 1974, of the deaths of four workers in the industry believed attributable to VCM exposure. Since that time angiosarcoma of the liver, a rare and fatal tumor, has been identified in at least 15 workers in U.S. PVC facilities. In addition, other forms of cancer, certain nonmalignant liver diseases, and acroosteolysis, a unique occupational disease, also have been found in workers within the industry (1).

Preliminary monitoring of VCM levels in ambient air at a number of VCM/PVC facilities was then carried out by the EPA. Levels ranging from <0.05 to 33 ppm were found, with about 10 percent >1 ppm (1 to 8 ppm). Integrated 24-hour samples generally contained 1 ppm or less (1). In this same study, measurements of VCM contained in sludge from the polymerization process reactor kettles ranged from <1 to as high as 3520 ppm. It is likely that this VCM is released into the atmosphere at the landfills at varying rates which depend on a number of factors such as the nature of the earth and debris cover under which the sludge is buried, the temperature of the sludge deposit, the thickness of the sludge layer, etc. Both municipal and industrial waste disposal sites of the dump or landfill type are involved in the disposal of these industrial wastes. Thus it was decided by the EPA that a need existed to investigate VCM emissions from PVC sludges and typical disposal sites representing a cross section of climate conditions, disposal methods, and contiguous population densities. Consequently the present study was initiated as a preliminary, low-level effort, to determine approximate VCM concentrations in landfill air and to perform initial measurements, in the laboratory and under controlled conditions, on the rates at which VCM is released from PVC sludges.

POLYVINYL CHLORIDE PRODUCTION

PVC, commonly known as vinyl plastic, is produced from VCM, a colorless, faintly sweet smelling gas. VCM is converted to solid PVC by one of four different batch polymerization processes. U.S. PVC production for 1974 was about 4.75 billion pounds (2). The processes used and the percentages of total production they represent are listed in Table 1.

TABLE 1. PVC PROCESSES

Process Type	Polymerization Medium	Percent of Total PVC Production
Suspension	Water	78
Emulsion	Water	12
Bulk	Monomer	6
Solution	Organic Solvent	4

Regardless of the process used, a typical PVC plant includes the following operations:

(1) Receiving and storage of VCM and catalysts
(2) Polymerization of VCM: measuring, charging, and reaction
(3) Stripping and recovery: reactor blowdown and recovery, and slurry handling and storage
(4) Centrifugation or filtration
(5) Drying
(6) Pneumatic conveying and storage
(7) Packaging and shipping
(8) Blending
(9) Waste treatment.

We are interested here only in those steps (4 and 9) of the PVC production process which result in by-product wastes containing suspended solid matter and VCM. Since most PVC is produced in aqueous media (Table 1) these by-product streams consist basically of water suspensions of fine, particulate PVC containing small amounts of various polymerization processing aids, and dissolved and/or absorbed VCM. It is this entrapped VCM which is of concern in the present study.

The aqueous waste streams are treated in various ways at different PVC plants. Basically the processing consists of steps to concentrate the solids content of the waste as much as possible while discharging waste water of acceptable quality to the local water treatment system, or natural outlets such as rivers. The processing includes chemical treatments to coagulate and sediment the solids and physical separation procedures such as large, specially designed settling and concentrating tanks and specialized centrifuging and filtration procedures. The final waste material is a water-based sludge ranging from about 15 to 40 percent solids. Physically these sludges range from waterlike, thin slurries to thick pastes approximating the consistency of a concrete premix.

These PVC sludges are industrial waste matter which could be used or disposed of in various ways. At the present time most, if not all, of these sludges, are discarded at municipal or privately owned landfills. Typically the sludges are transported to the landfill in pressure-controlled tank trucks or open-bed trucks and dumped into bulldozer-prepared pits or trenches that are 0.6 to 3 or more meters deep. They are then covered with compacted layers of trash and soil to a depth of 0.3 to 1 meter or more.

SAMPLE COLLECTION

Arrangements

At the beginning of this study three PVC plant site/landfill combinations were selected for sampling purposes. These combinations were chosen to provide good cross-sections of geographical location and climate, PVC plant technology, sludge type, and landfill practice. The protocol established for sample collection included the following steps:

(1) Visit to PVC plant by EPA and Battelle personnel
(2) Tour of PVC sludge processing, isolation, and storage facilities
(3) Observations of PVC sludge collection by waste hauling company
(4) Collection of PVC sludge samples for VCM analysis
(5) Follow sludge hauling truck to landfill with PVC company and/or hauling company personnel
(6) Meet landfill operating personnel and gain access to landfill

(7) Collect background air grab sample before PVC sludge disposal
(8) Observe PVC sludge disposal practice
(9) Collect air and sludge samples during disposal
(10) Collect air samples after PVC sludge disposal and coverage
(11) Collect air samples at same landfill site approximately 1 day later.

Air Samples

Grab air samples were collected at landfills before, during, and after sludge disposal and coverage, downwind of the known VCM emissions sites. The samples were collected in preevacuated (10^{-8} torr at 150 C) 3.5-liter stainless steel cylinders by opening the entrance port at normal breathing levels. The date, time, weather, and wind conditions were recorded for each sample taken.

Sludge Samples

During this study samples of the PVC sludges were collected both at the plants and at the landfills. Sludge collections at the landfill were done during the actual disposal operation except at Landfill 1 where sludge was collected both after disposal and after bulldozing and partial coverage. Sludge samples were collected in tightly sealed glass containers to prevent VCM evaporation, returned to the laboratory and stored at 5°C until analysis could be performed.

ANALYTICAL METHODS

The standard equipment used for VCM analysis in this study was a gas chromatograph-flame ionization detector (GC-FID) apparatus. Seven crosschecks were performed using a mass spectrometer (MS), with excellent agreement found. Grab air samples were analyzed directly, by injection of air aliquots into the GC-FID or, in one case, the MS. Headspace and liquid phase portions of PVC sludge samples were also analyzed by direct injection into the GC-FID or MS. PVC sludges were rountinely analyzed for VCM content by extraction with tetrahydrofuran (THF) and injection of an aliquot of the THF extract into the GC-FID (1). One direct analysis of a PVC sludge sample was also performed using the MS.

VCM Concentrations

VCM concentrations are expressed in parts per million (ppm). VCM concentrations in air are based on a volume ratio, or microliters of VCM per liter of air. Thus 1 ppm equals 1 µl VCM/liter of air. However, VCM concentrations in PVC sludges are based on a weight ratio, or micrograms of VCM per gram of sludge. Thus 1 ppm VCM in sludge equals 1 µg VCM/gram of sludge. Consequently, ppm VCM in air cannot be compared directly with ppm VCM in sludge. However a one-gram sludge sample analyzing 1 ppm VCM will yield 0.391 µl (STP) of VCM gas. Release of the VCM in 2.56 grams of this sludge into 1 liter of air would produce 1 ppm in air.

VCM Analysis by GC-FID

The analyses were done on a Packard Series 800 gas chromatography instrument using the following conditions:

Column - Porapak Q in an 8' x 3/16" stainless steel tubing
Temperatures - Column 120°C, Detector 120°C, and Injector 120°C
Flows - Nitrogen Carrier 30 ml/minute; Air 300 ml/minute; Hydrogen 30 ml/minute
Electrometer - 500 volts; 1×10^{-10} amps
Sample Injection - Hypodermic syringe septa and six way gas sampling valve
Detector - Flame ionization.

The GC was calibrated using commercial (Matheson Gas Co.) standards of VCM in nitrogen, supplied with a certified analysis. These were reanalyzed in our laboratory by MS. One standard contained 20.5 ppm VCM in nitrogen and the other 0.45 ppm. The 20.5 ppm standard was used routinely for this work.

In addition, a mixture of saturated and unsaturated hydrocarbons including methane, ethene, acetylene, ethane, propane, propene, isobutane, 1-butene and n-butane was chromatographed. Also individual samples of dichlorodifluoromethane (Freon 12), isobutylene and 1,3-butadiene were chromatographed separately. The total set of compounds chromatographed and their retention times in comparison to VCM are listed in Table 2.

TABLE 2. RESOLUTION OF VCM FROM POTENTIAL CONTAMINANTS

Compound	Formula	Retention Time, minutes
Methane	CH_4	0.6
Ethene	C_2H_4	1.0
Acetylene	C_2H_2	1.0
Ethane	C_2H_6	1.1
Propene	C_3H_6	2.8
Propane	C_3H_8	3.1
Freon 12	CCl_2F_2	3.7
VCM	$CH_2{=}CHCl$	5.7
Isobutane	$CH(CH_3)_3$	7.9
1-butene	$CH_2{=}CHCH_2CH_2$	8.7
Isobutene	$CH_2{=}C(CH_3)_2$	8.8
n-butane	$CH_3CH_2CH_2CH_3$	9.9
1,3-butadiene	$CH_2{=}CHCH{=}CH_2$	18.3

Freon 12 and isobutane have the nearest retention times to VCM of the thirteen compounds listed. However even these two compounds show differences in retention time of 2 minutes or longer, which is a substantial difference resulting in total separation of the elution peaks.

VCM Analysis by MS

The MS used for the crosscheck of the VCM analyses was a Consolidated Electrodynamics Corporation Model 21-620, equipped with a calibrated inlet system specially designed for gas analysis. Inlet sample pressure is measured using a micromanometer. Ionization conditions used were 50 volts at 40 milliamps. Pure VCM was used for calibration so that standardization of the GC and MS were completely independent.

Seven MS verification analyses were performed during this study to confirm GC analysis of VCM. These are summarized in Table 3.

TABLE 3. CROSSCHECK VCM ANALYSES BY MS

Sample	VCM, ppm	
	MS	GC-FID
1, Sludge, Vapor Phase	2,200.	2,700.
2, Sludge, Vapor Phase	2,300.	1,900.
3, Landfill Air	0.05	0.07
4, Sludge, Dry Solids	210.	200.
8, Plant Stream Liquid	23,000.	28,000.
9, Plant Stream Vapor	8,600.	8,600.
10, Plant Stream Vapor	30,900.	37,400.

DISCUSSION

In the following sections data obtained on VCM concentrations in air samples and PVC sludge vapor, liquid and solid phases are discussed. Also the results of a very preliminary study of VCM release rates from PVC sludges are discussed. Finally a brief analysis of the VCM emissions potential of the sludges is presented.

Grab Air Samples

The results of laboratory analysis of grab air samples collected at three landfills are listed on the following page in Table 4.

VCM concentrations ranging from 0.07 to 1.10 ppm were found at normal breathing levels at three landfills. At Landfill 1, the levels found were relatively low and the spread in concentrations was quite small (0.07 to 0.11 ppm). At Landfill 2 concentrations ranging from 0.13 to 0.49 ppm were found while concentrations found at Landfill 3 ranged from 0.16 to 1.10 ppm. Three important features of these data are noted. First, there appears to be a VCM background level of about 0.1-0.3 ppm in the air at all three landfills. Secondly, instantaneous VCM concentrations as high as about 1 ppm are on occasion observed, even as long as 24 hours after the PVC sludge is buried under compacted soil. The third observation concerns an air sample which was collected about 5 cm from a stream of liquid sludge discharging from a truck during landfill disposal. This air sample was, in effect, "spiked" with extra VCM. The fact that this particular air sample showed an appreciably higher VCM analysis (1.90 ppm) than the other air samples collected at the same landfill provides good indirect proof that the VCM peaks in the chromatographs of landfill air are correctly identified.

Sludge Samples

The PVC sludges were analyzed to determine VCM contents. The vapor phase (head space) and liquid filtrate portions of the sludge samples were analyzed first. It was determined that the amount of VCM in both these phases was <10 percent of the total VCM in all seven sludges. In fact the VCM content of these phases was <1 percent of the total sludge VCM content with even moderately high total VCM

TABLE 4. VCM CONCENTRATIONS IN GRAB AIR SAMPLES TAKEN AT LANDFILLS

Air Sample Number	Collection Information				VCM[†], ppm
	Temp, °C	Weather	Wind Velocity, kph*	Sampling Location	
Controls		Analysis of laboratory air grab samples			<0.01
			Landfill 1		
1	14	Very cloudy	0-8	30 meters from disposal site just before sludge dump (date 4/24/75)	0.11
2	14	Very cloudy	0-8	At leading edge of freshly dumped sludge (4/24/75)	0.10
3	14	Very cloudy	0-8	30 meters from disposal site after dumping and dozing (4/24/75)	0.07[††]
			Landfill 2		
4	17	Very cloudy, raining	5-11	At disposal site before sludge discharge started (6/12/75)	0.13
5	17	Very cloudy, raining	5-11	Edge of sludge pit as soon as discharge is completed (6/12/75)	0.13
6	16	Cloudy	3-11	At previous days disposal site before fresh discharge (6/13/75)	0.27
7	16	Cloudy	3-11	About 5 centimeters from sludge discharge stream (6/13/75)	1.90
8	23	Partly cloudy	0-8	Edge of sludge pit during second dump (6/13/75)	0.30
9	23	Partly cloudy	0-8	Edge of sludge pit during third dump (6/13/75)	0.12
10	29	Very cloudy	8-16	180 meters inside landfill, near sludge disposal area (8/18/75)	0.49
			Landfill 3		
11	22	Partly cloudy	5-11	30 meters from disposal site before sludge discharge (6/24/75)	0.16
12	23	Partly cloudy	5-11	Edge of sludge pit between two trucks, while both are discharging (6/24/75)	0.40
13	23	Partly cloudy	5-11	Same as (12) near the end of the discharge period (6/24/75)	1.03
14	23	Partly cloudy	5-11	30 meters from disposal site after sludge pit is covered (6/24/75)	0.16
15	21	Partly cloudy	0-8	Standing over previous days covered disposal site (6/25/75)	0.17
16	26	Partly cloudy	0-8	Same as (15) (6/25/75)	1.00
17	27	Partly cloudy	0-8	Same as (15) (6/25/75)	1.10

[*] Wind velocity in kilometers per hour measured with an anemometer.

[†] Gas chromatography with flame ionization detector (GC-FID).

[††] This sample was also analyzed by MS as a crosscheck and 0.05 ppm were found.

contents (≥200 ppm, dry solids). Thus the amount of VCM in these two phases is negligible in terms of potential landfill VCM emissions.

VCM Contents of Sludge Solids

The PVC sludges were filtered and the sludge solids subjected to VCM analysis as described earlier. The results obtained are shown in Table 5.

VCM concentrations found in the sludge samples ranged from 7 to 520 ppm in the wet filtered sludge, and from 20 to 1260 ppm on a dry solids basis. These concentrations can be compared with the values found in EPA studies (1) in the spring of 1974 at six PVC plants. In that work, VCM concentrations found ranged from <1 ppm to 3520 ppm in wet sludge and from <1 ppm to 4200 ppm in dry sludge but with most of the samples containing >10 ppm on either a wet or dry basis. Thus the VCM concentration range found in the present work is similar to that observed in the earlier studies, although the highest concentration level found in the present work is about 7 times lower than the highest values found by the EPA workers in the spring of 1974.

VCM Release Rate Studies

Release rate studies were performed using the apparatus shown in Figure 1.

Release rate experiments were performed on PVC sludge Sample 2. This sludge was used since the VCM concentration was in the middle range. Release experiments were conducted at 25°C using 13 to 15 grams of sludge. This provided a layer about 1.3 cm deep in the release rate apparatus. In release experiment 2 an equal thickness layer of loam soil was placed over the sludge. A 30 cc/minute air flow was passed

TABLE 5. VCM CONCENTRATIONS FOUND IN PVC SLUDGES

	PVC Sludge	Weight Percent Solids		VCM Concentration,* ppm by weight	
No.	Identification	As Collected	After Filtration	Wet Sludge	Dry Solids
		Plant 1			
1	Freshly centrifuged sludge[†]	34	42	150	360
2	Fresh combination sludge[††]	--	55	210	380
3	Sludge from full truck[x]	35	41	520	1260
4	Sludge freshly dischared from truck[y]	34	42	90	200
5	Sludge after disposal and doze	36	41	90	200
		Plant 2			
6	Sludge collected during discharge from truck[y]	17	40	7	20
		Plant 3			
7	Sludge collected during discharge from truck[y]	30	60	90	130

* VCM analysis of wet (filtrated) sludge by GC-FID analysis of THF extract. Also calculated on a dry solids basis. 360 ppm = 360 μg/g = 0.36 mg/g = 0.036 weight percent.

[†] Sludge collected at PVC plant directly from centrifuge discharge tube.

[††] Sludge collected at PVC plant from partly filled truck loader.

[x] Sludge collected at PVC plant from full truck loader.

[y] Sludge collected during landfill disposal.

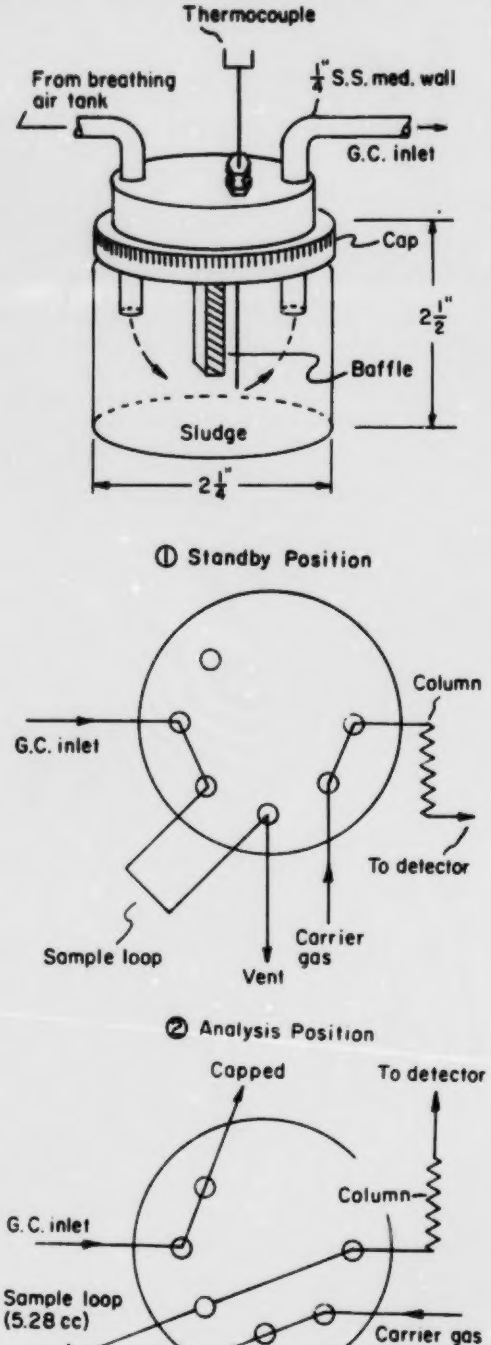
Thermocouple
From breathing air tank
1/4" S.S. med. wall
G.C. inlet
Cap
2 1/2"
Baffle
Sludge
2 1/4"
① Standby Position
Column
G.C. inlet
To detector
Sample loop
Vent
Carrier gas
② Analysis Position
Capped
To detector
Column
G.C. inlet
Sample loop (5.28 cc)
Carrier gas

FIGURE 1. VCM RELEASE RATE APPARATUS

over the sludge. This gas flow rate is equivalent to a no wind (calm) day at a landfill (~ 0.002 kph wind velocity). It is under these conditions that maximum VCM concentrations might be expected to accumulate at landfills. The VCM concentrations are instantaneous values obtained by injecting a 5.28--cc portion of the constantly outflowing air into the GC apparatus. The release rate data collected are plotted in Figure 2.

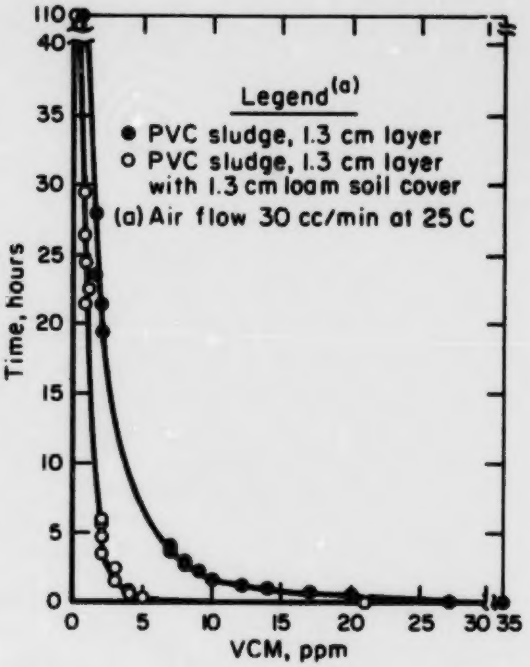

FIGURE 2. VCM RELEASE RATE FROM PVC SLUDGE

The VCM release curves are similar in form to those recently reported by Berens (3) for dry PVC powders which consisted of a mixture of particle sizes and types including relatively large particles, e.g., 40 μ fused, glassy agglomerates, even though Berens' work was done using very small samples (100 to 500 mg) at very low pressures (0-100 torr). Berens' VCM release rates, initially rapid, slowed dramatically in a few minutes to rates indicating that times on the order of an hour or more would be required for all VCM to be released. This was in contrast to small (4 μ) uniform particle size PVC powders which yielded all absorbed VCM in 1 or 2 minutes. This indicates that the PVC sludges may consist mostly of relatively large PVC particles or fused particle agglomerates. However the slower absolute VCM release rates observed in the present work are probably more due to the relatively thick samples and the very low air flow rate over the sludge surface.

The absolute amounts of VCM represented by the curves of Figure 2 were determined by mechanical integration of the areas under the curves. This was done by tracing the curves on uniform weight tracing paper. The curve areas were cut out and weighed analytically (± 0.1 mg). A reference area was also weighed. The VCM equivalent of a unit weight was calculated by multiplying ordinate VCM concentration in cc VCM/cc air by abcissa values expressed as air volumes (30 cc/min x 60 min/hr x number of hours). Then mg VCM = (cc VCM) (2.556 mg VCM/cc). The amounts of VCM found are given in Table 6 expressed as percentages of the total VCM content of the given sludge sample.

TABLE 6. FRACTION OF VCM AVAILABLE IN SLUDGE SAMPLES RELEASED IN SPECIFIED TIME INTERVALS

	Sludge		Percent VCM Released			
			Time Interval, hr			
Run	Grams	VCM, mg	2	8	24	110
1	13.6	2.86	5	16	25	32
2	13.3*	2.79	2	5	8	11

* 1.3 cm loam soil cover.

The results obtained indicate that a minor portion of the VCM in PVC sludge may be quickly released at the landfill but that a major portion of the VCM is released very slowly over a long time period. This means that as PVC sludge is disposed, absolute amounts of VCM will probably continue to rise for a long, indeterminate period until a "quasi-steady-state condition" is reached. At this point continuous, slow evolution of VCM will probably occur for a long time after sludge is no longer disposed of at the landfill. This conclusion is consistent with the finding that a VCM air concentration in the range of 0.1 to 0.3 ppm was found at each landfill.

VCM Emissions Potential

The VCM emissions potential of the PVC sludges was calculated based on the VCM concentrations in Table 5 and data supplied by the PVC companies on the amounts of PVC sludge being disposed of at the landfills. The results of these calculations are shown in Table 7.

TABLE 7. POTENTIAL VCM EMISSIONS FROM LANDFILLS BASED ON COMPANY SUPPLIED PVC SLUDGE DISPOSAL RATES AND ANALYTICAL VCM CONTENTS

PVC Sludge Number	PVC Dry Sludge Solids Disposal Rate, kg/day	Dry Sludge VCM Content, mg/kg	VCM, Daily Disposal Rate kg	VCM, Daily Disposal Rate liter*
		Plant 1		
3	4,626	0.00126	5.83	2,285
4	4,490	0.00020	0.90	353
		Plant 2		
6	2,948†	0.00002	0.059	23
		Plant 3		
7	172††	0.00013	0.022	9

* (kg VCM)(10^3)(24.5 l/mole)/(62.5 g/mole).

† Company supplied figure - 35,000 gal/wk. Dry solids based on 159,110 L/wk and 1.1 kg/liter.

†† Company supplied figure - 4,000 gal/mo. Dry solids based on 18,184 L/wk and 1.1 kg/liter.

The amount of VCM being disposed of at the landfills thus varies between 0.022 and 5.83 kg or 9 and 2,285 liters on a per day basis. However, it is pertinent to note that industry is actively investigating processing improvements that may reduce the amount of VCM in these sludges in the future and is looking at alternate disposal and recycle schemes. This should help reduce the VCM concentration in sludge in the future. Unless eventual increases in PVC production offset these future decreases in VCM concentrations, it can be anticipated that the total amounts of VCM being disposed of will eventually decline.

CONCLUSIONS

The following conclusions are indicated by the findings of this study:

(1) A background air concentration of about 0.1 to 0.3-ppm VCM appears to be present in air at landfills where PVC sludge has been disposed of for several years.

(2) Instaneous VCM air concentrations on the order of 1.0 ppm can occur at normal breathing heights (~1.5 meter) above ground level at these landfills as long as 24 hours after PVC sludge deposits are covered.

(3) Prevailing landfill air temperatures, and presumably ground temperatures as well, appear to influence VCM release rates.

(4) Time-weighted average sampling (15-minute, 8-hour, 24-hour) is required to determine whether concentrations of VCM in air that pose a health hazard occur either at the landfills or in adjacent residential or public access areas.

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DISPOSAL OF WASTE OIL RE-REFINING RESIDUES BY LAND FARMING

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ABSTRACT

In the Spring of 1974 the Environmental Protection Agency undertook the removal and disposal of approximately 1,700,000 gallons of residues from a waste oil re-refining plant. The waste was stored in unsafe lagoons near Ogden, Utah, that threatened a waterfowl refuge and was responsible for the loss of numerous migratory waterfowl that landed in the lagoon. It was decided to dispose of the oil-water emulsion portion of the lagoon contents in a land farm. The paper discusses the evaluation of disposal alternatives, criteria used for selecting a suitable site, methods of applying and treating the oil-soil system, and methods for monitoring and evaluating the project. This project was conducted in a semi-arid area and employed supplemental fertilization. After one year, oil degradation on fertilized plots approached 80 per cent.

INTRODUCTION

In the summer of 1973, Region VIII of the Environmental Protection Agency became aware of a serious oil pollution problem in a makeshift lagoon near Ogden, Utah. The lagoon was adjacent to an irrigation return canal that flowed directly into the Weber river delta which comprised a portion of the State of Utah operated Ogden Bay Migratory Bird Refuge. The flow from this area then discharged into the Great Salt Lake, three miles distant from the lagoon. Much of the initial notoriety of the problem involved migratory waterfowl in the flyways to the bird refuge landing in the oil lagoon and becoming fatally distressed. In addition the lagoon was constructed without any attention to safe design and posed a potential water pollution hazard if the weakened dikes of the lagoon failed.

The lagoon was located at the site of a small-time marginal auto salvage yard and contained numerous scrapped vehicles and miscellaneous auto parts along with the oily waste. The oily waste in the lagoon came from an oil re-refining operation of the Western Petroleum Company who operated a facility in Ogden. The re-refiner was primarily involved in reclaiming waste journal box and crank case oils collected from the Union Pacific Railroad along with waste oil collected from other local sources. The lagoon contained residuals from this re-refining process which consisted of an acid sludge containing spent filter clay, up to 30% unrecovered processed oil and various amounts of lead and engine and bearing metals which had accumulated in the feed stock. Some of the waste had been disposed of on Union Pacific property and right-of-way in the Ogden area prior to 1967. The remainder of the waste was disposed of in lagoons on the re-refiner's property in Ogden, but these lagoons were discovered to be polluting the nearby Weber River. In 1967, the lagoon site in question was leased from the auto salvage yard and a cut and fill disposal operation began. This technique seemed to be satisfactory for the first nine months of operation but the waste production from the re-refiner increased to such a rate that they were unable to conduct the operation in the originally intended manner, and a lagoon then was quickly constructed by erecting temporary dikes across drainage lines on the property. The lagoon was used until 1972 when the lease on the disposal site expired and the lagoon was then abandoned. Upon abandonment the lagoon covered approximately five surface acres contained about 1,200,000 gallons of liquid and an estimated 10,000 cubic yards of acid sludge.

The lagoon contents were in three distinct layers. The top layer contained 750,000 gallons of a tight oil-water emulsion at a pH of 2.5-3.0 and a moderately high concentration of heavy metals such as lead which ranged from 3 to 400 micrograms per gram. The middle layer was 450,000 gallons of pH 1.0-3.0 water which probably came from surface waters and ground water percolation at the site. The high pH was probably due to waste sulfuric acid. The bottom layer was a highly acid sludge of pH 1.0 and had a very high heavy metals concentration with lead values of 11,000 micrograms per gram.

As a result of EPA actions under section 311 of the Federal Water Pollution Control Act and related Federal court orders, EPA was directed to conduct an oil removal and disposal operation to eliminate the pollution threats at the site. The most perplexing part of the operation was to be the satisfactory disposal of the material removed from the lagoon. The Federal On-Scene Coordinator for the project, George Rice of EPA's Region VIII office in Denver, conducted an exhaustive review of disposal and/or reuse alternatives. Possible reuse of the lagoon oils for roofing materials, coking, or asphalt yielded negative responses as did the possibility of blending with crude oil feed stocks at local refineries. Blending with residual oils as fuels was also considered but concerns about low BTU values and the requirements to capture potential air emissions of heavy metals such as lead discouraged this alternative. Incineration was also examined as an alternative but the high water content of the tight oil emulsion and the need for satisfactory capture of any lead emissions resulted in this alternative being rejected. The next obvious step was a thorough review of potential land disposal alternatives.

One of the initial land disposal alternatives considered was the use of landfills. This alternative was a difficult one because of the high ground water table that exists in the areas near the Great Salt Lake. Much of the land is very low with poor drainage and standing water during wet seasons. The use of the oil as a dust control agent for rural roads or as mix with sand and gravel for such roads was also considered but the potential problem of heavy metal and oil migration during periods of precipitation was a negative factor. The search now seemed to narrow to the alternative of land farming as a means to safely contain and degrade the oil mixtures from the lagoon.

The paper will now discuss the factors surrounding the selection of a suitable site, the design criteria for the site, the disposal operation, the scientific monitoring at the site, and future plans for the site.

SITE SELECTION

When it appeared that land farming was going to be the disposal method, prospective sites had to be selected and evaluated. The sites would have to be in the general vicinity of the lagoon so that transportation costs could be kept to a minimum, the topography would have to permit adequate drainage control, soil characteristics would have to be suitable for good drainage and microbial activity, and, perhaps most important, the owners of the site had to give their permission and local officials (including neighbors) had to be willing to allow the project to take place.

From the technical and economic point of view three possible sites were evaluated. One site offered by the Union Pacific Railroad was flat and alkaline but was only 10 feet higher than the Great Salt Lake which meant strong ground water influence. It was also an attractive duck hunting area. Trading one water-fowl problem for another potential one would not have been wise. The State of Utah offered a site, but it was even lower in elevation than the railroad offer and was saline; so that site was deemed unsuitable.

The third site was under the control of Hill Air Force Base, Ogden, Utah, and was located 1-1/2 miles west of the oil lagoon. There were areas of satisfactory soil depth and gentle to 5% slopes. Drainage from the area was directed toward a quarry where runoff could be controlled and monitored. Soil properties had been grossly characterized in surveys published by the Department of Agriculture Soil Conservation Service. The soil was non-agricultural and soil texture appeared excellent from the standpoint of adequate aeration and structure. The elevation ranged 30 to 120 feet above the level of the Great Salt Lake. This site had no special use at that time and was concluded to be very desirable. The next step was to obtain the necessary approvals and clearances.

One of the primary tools available to a Federal On-Scene Coordinator for managing an oil or hazardous chemical spill incident is the National Oil and Hazardous Substances Pollution Contingency Plan (1). This plan establishes a framework for regional contingency plans and a Regional Response Team (RRT) which is made up of representatives of Federal and State agencies that have a key role or interest in the spill incident. This RRT was effectively used throughout all phases of the Odgen Bay lagoon project and it was very helpful in obtaining necessary approvals for the land farm. The State of Utah's Division of Health worked directly with EPA on investigating sites which streamlined their approval of the site. The Department of Defense is one of the primary agencies under the National Contingency Plan and this facilitated good communications with local Air Force officials. The pollution problems of the lagoon received extensive local press coverage, especially the distressed ducks and other waterfowl, and many local officials and agencies were anxious to be part of the solution. EPA assured the Air Force that after two years no significant land use restrictions were anticipated at the site, other than the possible prohibition of cattle grazing. The Air Force and EPA then entered into an agreement to use the site.

SITE DESIGN AND PREPARATION

Site Design Considerations

To develop an adequate design for the project and to assist in disposal operations EPA contracted with Dr. John S. Skujins, Associate Professor of Soil Biochemistry and Microbiology at Utah State University. Representatives from EPA research laboratories, EPA regional and headquarters spill control staffs, the State of Utah, and local county officials also contributed to this phase. It was assumed that the soil would have to be enriched to provide adequate nutrients for good microbial degradation and the alkaline level would have to be increased to neutralize the acidic oil emulsion. Most soils in Utah are alkaline in nature and would have simplified the neutralization phase, but the Little Mountain site was a Utah rarity, acid soil. The primary reference for determining the feasibility of land farming and establishing initial design values was an EPA funded project with Shell Oil Company in Deer Park, Texas, on the disposal of oily refinery waste by soil cultivation (2). One of the primary objectives of the Shell project was to reapply waste to an oiled plot as soon as the degradation process had progressed sufficiently to permit the added waste load. They also benefited from the long growing season in the Houston area and the plentiful rainfall. The Ogden Bay project had design constraints of maximum loading on a one-time application in an area with less than 12 inches annual rainfall; a cold, wet winter season followed by a dry, hot summer season; and the requirement to return the site to as many original uses as possible.

The use permit for the site covered approximately 200 acres on the south slope of Little Mountain, of which only 40 acres were found suitable for oil application because of slope limitations, soil depth requirements, rock outcroppings, and pre-existing roads (Figure 1). Plots were laid out and staked by Dr. Skujins and then individually surveyed and mapped (Figure 2). Base line soil samples were taken and comparative analyses made by Ford Laboratories, Salt Lake City, and by the Ecology Center, Utah State University.

On the basis of the background analyses and the projected oil application rate required to dispose of the lagoon contents, the quantities of lime, phosphorus, and nitrogen to be added were calculated (Table 1). The governing design assumption was the application rate for the oil emulsion phase. Using previous studies and limited field and laboratory tests, a rate of 10,800 gallons of oil/acre for a six inch soil tilling depth was selected. This rate was for oil alone and did not include the water phase of the emulsion. In order to keep an accurate record of total oil applied to a plot, the water content of the emulsion-water mixture spread on the plots would have to be determined at frequent intervals.

The application rates and procedures recommended by Dr. Skujins were guides set up with the realization that limitations of equipment, time and money could result in considerable modification of these guidelines. Varying combinations of oil and nutrient application rates between the plots were chosen to provide information for later phases of this project as well as guidance for other land farming projects.

Site Preparation

Soil depth within the designated farm plots ranged from 6 to 20 inches, with several rock outcroppings occurring randomly throughout the area. The entire farm was ripped using a D-8 Caterpillar dozer and a Caterpillar C-12 road grader with a scarifier. Quantities of medium to large size rocks on the surface unearthed during this operation were removed by hand labor. After ripping and rock picking had been completed, the entire area was cultivated to a depth of approximately five inches by disc or barber-shank harrow action. Both disc and harrow were suspended by a three-point hitch and worked effectively in the shallow tilling operations required of them. However, the barber-shank harrow proved better during rock encounters due to its ability to pass the rock between the teeth where the disc would have to step over.

Plans then called for complete application of lime and soil nutrients to the farm before depositing lagoon liquids. Lime nutrients were applied to plots A through N (see Figure 2) using a standard agricultural spreader. The plots were cultivated again after the application of lime and nutrients to provide good mixing prior to the application of the oil emulsion. No additives were applied directly to plots O, P, Q, and R.

In order to prevent runoff of the oil after application, the road grader was used to establish 12 inch high berms around the perimeter of the plots. Straw bales were also considered for this function, but a shortage of straw in the area discouraged this alternative. Using the grader turned out to be much quicker and cheaper.

SITE OPERATION

Spreading and Distribution

Two tank trucks normally used for dust control in highway construction were used for transporting and spreading the emulsion at the land farm. Emulsion liquids were top loaded into the transport tankers using a Crisifulli centrifugal pump and a field erected loading arm. Liquids were discharged from the tankers onto the prepared plots through a 12-inch rear, gravity feed, exit port onto a horizontal splash pan suspended 10 inches below the port. The emulsion liquids were spread as uniformly as possible on the designated plots. The application rate was gauged by comparing the tanker volume to the area covered at a given truck speed. One of the trucks was a converted military 6 X 6 and was able to operate over a wide speed range in the plowed field. The other truck was a con-

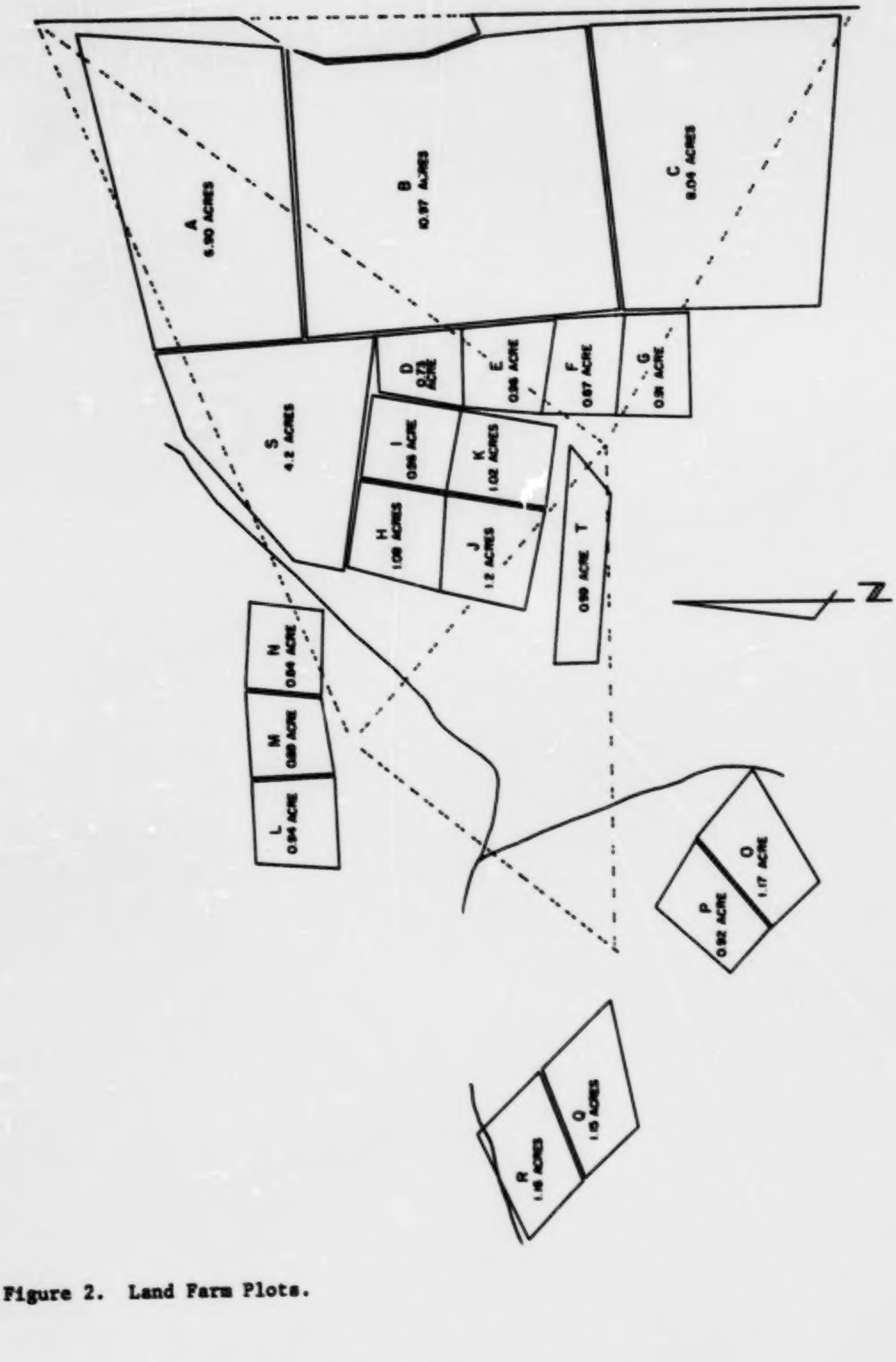
A
6.90 ACRES
B
10.97 ACRES
C
8.04 ACRES
D
0.73
ACRE
E
0.96 ACRE
F
0.87 ACRE
G
0.31 ACRE
S
4.2 ACRES
I
0.96 ACRE
K
1.02 ACRES
H
1.08 ACRES
J
1.2 ACRES
T
0.90 ACRE
N
N
0.84 ACRE
M
0.89 ACRE
L
0.94 ACRE
P
0.92 ACRE
O
1.17 ACRE
R
1.16 ACRES
Q
1.15 ACRES

Figure 2. Land Farm Plots.

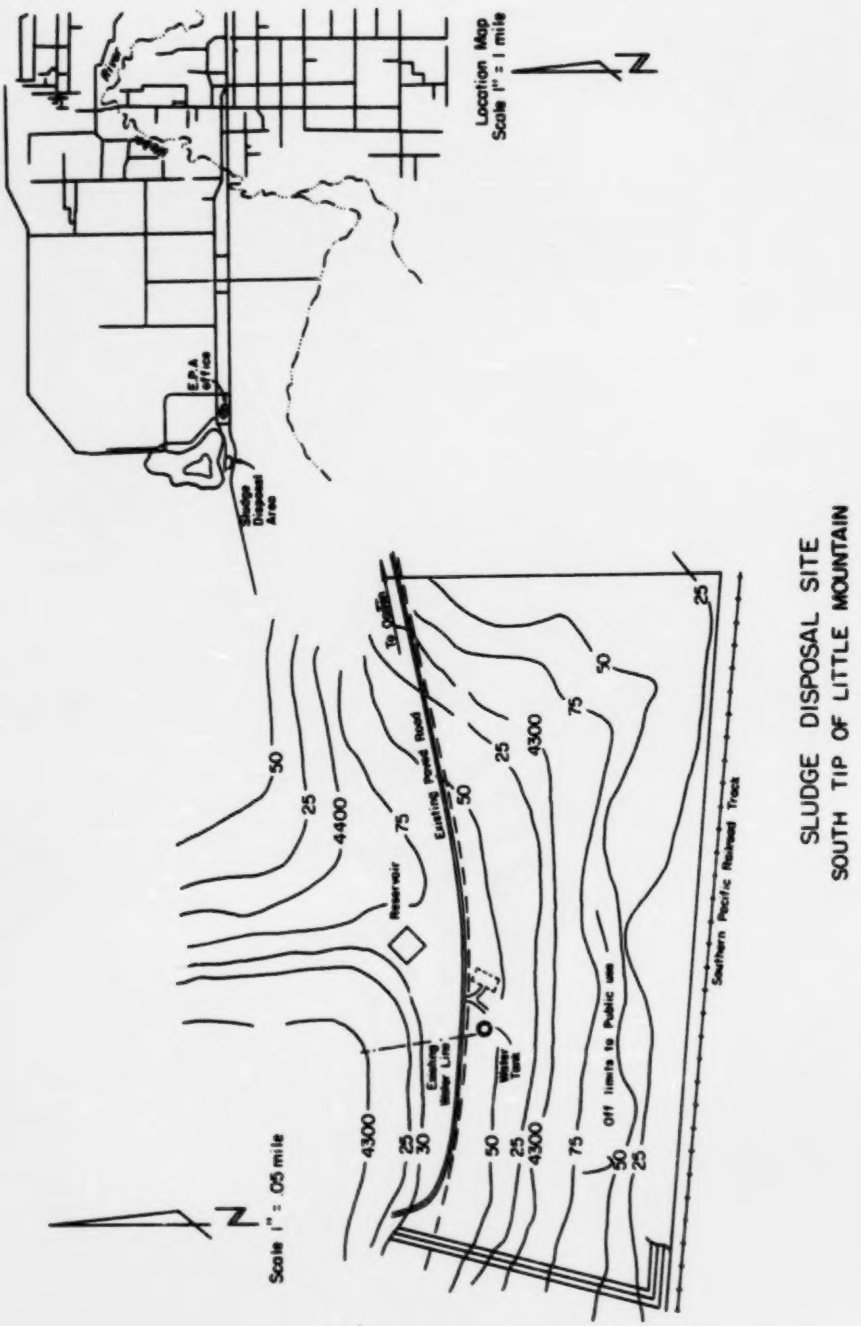
Location Map
Scale 1" = 1 mile
N
E.P.A. Office
Sludge Disposal Area
River
SLUDGE DISPOSAL SITE
SOUTH TIP OF LITTLE MOUNTAIN
Southern Pacific Railroad Track
Off limits to Public use
Water Tank
Existing Water Line
Reservoir
Existing Paved Road
To Ogden
Scale 1" = .05 mile
N
4400
4300
75
50
30
25

Figure 1. Little Mountain Site Plan.

TABLE 1. SUGGESTED APPLICATION RATES

Plot Designation	Area Acres	Material	Amount of Material per Plot	Pure $Ca(OH)_2$ 1)	C/N Ratio	Theoretical N	Urea 45% N	Theoretical P 2)	Application Rate
				kg		kg	kg	kg	
A	6.9	emulsion	75,700 gal	1200	20:1	5300	12,600	570	10,800 gal/6"/acre
B	10.97	emulsion	119,000 gal	1900	50:1	3310	7,370	330	10,800 gal/6"/acre
C	8.04	emulsion	86,600 gal	1400	50:1	2420	5,360	240	10,800 gal/6"/acre
D	.73	emulsion	7,884 gal	140	50:1	220	540	24	10,800 gal/6"/acre
E	0.96	emulsion	10,368 gal	140	10:1	1455	2,700	120	10,800 gal/6"/acre
F	0.87	emulsion	18,792 gal	250	20:1	1320	3,600	160	21,600 gal/6"/acre
G	0.91	emulsion	19,656 gal	250	50:1	550	1,340	60	21,600 gal/6"/acre
H	1.08	sludge	160 cu. yd.	2200	20:1	3890	8,000	360	60 metric tons/6"/acre
I	.96	sludge	160 cu. yd.	2200	50:1	1400	3,200	144	60 metric tons/6"/acre
J	1.2	sludge	190 cu. yd.	2200	50:1	1730	3,200	144	60 metric tons/6"/acre
K	1.02	sludge	160 cu. yd.	2200	10:1	7340	16,000	720	60 metric tons/6"/acre
L	0.94	emulsion	20,302 gal	350	20:1	1470	3,240	145	10,800 gal/6"/acre
M	0.84	emulsion	18,144 gal	300	50:1	508	1,200	54	10,800 gal/6"/acre
N	0.84	emulsion	18,144 gal	300	100:1	254	600	27	10,800 gal/6"/acre
O	app. 17	sludge	1000 metric tons	17,100	20:1	30,000	67,000	3,000	60 metric tons/6"/acre

1) Includes approximately 125 kg $Ca(OH)_2$ per acre 6" to stabilize soil pH
2) Should be applied as commercially available potassium phosphate. Theoretical value should be multiplied by 10 to obtain approximate commercial weight of weight of fertilizer (0-10-0).
3) 1 cc pure oil per 30 cc soil
4) 7.5% pure oil in soil

verted civilian highway vehicle and did not have a versatile speed range and occasionally had trouble negotiating the terrain. The field engineer exercised direct control of all truck movements to ensure, as nearly as possible, conformity with Dr. Skujins recommended application rates. The water content of the water-emulsion mixture had to be expeditiously determined in order for the field engineer to be reasonably certain of the amount of oil to be added to the plot. The normal test method would be a time consuming Soxhlet extraction but satisfactory results were obtained using a gravimetric procedure based on the principle of weight loss after drying. This procedure showed the water content in the emulsion mixture increased from approximately 50% in the lagoon to 60-65% after pumping and transport.

Plans originally called for the emulsion to lay on the surface after spreading to allow for short-term weathering in the hot sun before final cultivation. However, due to the mixing of the emulsion and aqueous phases by the truck loading pump, the liquids discharged from the truck were less viscous than expected and accumulated in the tire depressions and tended to run. On the first day of land spreading the threat of rain required that one of the tractors in use at the farm follow the tanker with the disc or harrow, mixing dirt and emulsion to hold it in place. This immediate cultivation was difficult because of the slippery conditions, but no oil was ever detected in runoff from the site.

As the mixed loads of emulsion and aqueous layers were pumped from the lagoon the proportion of the aqueous phase became greater and separated. The aqueous layer was decanted after load stratification during transport, and, after the emulsion started to flow, the air-actuated valve was closed and the remainder of the emulsion was spread on designated plots.

The total volume of liquids removed from the lagoon exceeded the original estimate of 1,200,000 gallons, and, eventually, 1,675,000 gallons of liquid was removed from the lagoon. This included approximately 721,327 gallons of emulsion and 905,510 gallons of aqueous phase which was spread on 40.85 acres, and 47,825 gallons of aqueous phase which was spread on farm roads for dust suppression (Table 2). After final liquid loads were placed and nutrient spreading completed, designated plots were tilled to a depth of 5 inches with an agricultural rototiller or cultivated with the barber-shank harrow.

Follow Up Site Operations

The liquid distribution and soil treatment operations at the land farm were completed in May 1974. The work plan called for remixing the soil with a rotary tiller in the Fall of 1974 and the Spring and Fall of 1975 to improve soil aeration. Additional applications of nitrogen in the form of urea were also planned with reseeding, if necessary, in the Fall of 1975.

In practice, the nutrient levels in the plots stayed at a satisfactorily high level in the Fall of 1974 and the soil was very friable indicating good aeration properties. Retilling and nitrogen addition was then delayed until Spring 1975. Reseeding was done in Fall of 1975 and additional tilling and nutrients were not needed at that time.

SITE MONITORING

In order to thoroughly understand the degradation process at the land farm and assess the degree of recovery of the land for reuse, EPA contracted with the Utah State University Ecology Center and their Departments of Biology and Soil Science and Biometeorology. This section of the paper is not a complete discussion of the study methods and results from the Utah State effort but is intended to provide the reader with a general summary.

Samples were taken from the established land farm plots and analyzed to determine soil characteristics, nutrient levels, heavy metals, pH, oil content, dehydrogenase activity, soil respiration, microbial activity, and microbial composition and density. A summary of the findings of the analyses of the samples and field observations follows.

The first sampling taken after application of the oil emulsion and fertilizers was June, 1974. At this time there was a triple increase in dehydrogenase activity

TABLE 2. LAND FARM APPLICATION RATES

Plot	Acres	Emulsion (gal/acre)	Aqueous (gal/acre)	Lime (lbs/acre)	Phosphate (20%) (lbs/acre)	Urea -'74 (45% N) (lbs/acre)	Urea -'75 (45% N) (lbs/acre)
A	6.90	16,030	2,730	800	250	1,180	735
B	10.97	19,740	1,590	930	250	1,180	735
C	8.04	14,350	2,050	935	250	1,180	735
D	0.73	23,030	11,080	935	250	1,180	960
E	0.96	23,030	11,080	935	500	2,360	1,540
F	0.87	25,660	14,930	1,680	750	3,540	2,425
G	0.91	25,660	14,930	1,660	250	1,180	850
H	1.08	23,920	14,620	1,900	500	2,360	1,430
I	0.96	23,920	14,620	1,900	500	2,360	1,465
J	1.20	23,920	14,620	1,900	750	3,540	2,700
K	1.02	23,920	14,620	1,900	750	3,540	2,345
L	0.94	19,520	13,519	1,670	750	3,540	2,095
M	0.84	19,520	13,510	1,670	500	2,360	1,675
N	0.84	19,520	13,510	1,670	250	1,180	840
S	4.20	9,780	11,020	-	-	-	-
T**	0.99	-	-	-	-	-	-
O-R	4.4	-	150,810*	-	-	-	-
Dust Control			47,825*				
Total	45.85	721,327	953,336				

- All plots tilled to a depth of five (5) inches.

* 50 lbs of lime for pH control was added to each truckload of aqueous solution as it was pumped from the lagoon.

** Contains approximately 630 cubic yards of oil-stained soil stripped from exposed surfaces of lagoon non-sludge contaminated bottom and perimeter areas.

compared to the activity before addition of oil indicating that the oil decomposition has begun. The samples taken in March, 1975, (the same season that control samples were taken before oil application in 1974) showed approximately 4 times as great an activity. The April and May samples of 1975 showed a gradual decrease in activity, as did the samples for the summer of 1974. The November 1974 analyses again showed an increase, probably due to the increase in moisture during the fall.

The soil respiration values doubled from March 1974 to June 1974. The amount of CO_2 released decreased in the summer of 1974, but in the fall the respiration rate more than tripled. High respiration levels indicate that the oil is being degraded, releasing excess CO_2. This sharp increase in overall soil respiration during the wet fall season may indicate more active microbial degradation at that time. The respiration decreased slightly in the March 1975 samples, and continued to show an overall decrease throughout the Spring. It is also significant that the untreated sampling site had a much lower rate of respiration than those plots treated with oil.

The chemical analysis of the soils shows that the heavy metal content has not changed over the year's time. The pH values for most of the plots have not changed appreciably over the year; they still average 6.9 to 7.7.

The percent phosphorous has remained about the same, but the percent nitrogen in the soil decreased about two-thirds by the end of 1974. The plots were recultivated and two-thirds of the amount of N applied in Spring 1974 was applied again to the plots in Spring 1975. It is interesting that the cation exchange capacity of the soil increased slightly. This is a good indication that more organic matter is being formed in the soil.

The total microbial numbers increased sharply in June 1974. This was probably a response to the water added to the plots along with the oil and fertilizers. There was a significant drop in total numbers during the summer 1974. This was a relatively hot, dry summer; therefore the microbial numbers were probably responding to a lack of moisture. The total aerobic numbers reached a level point in late fall of 1974, then apparently responded to the moisture from winter with another significant increase shown in March 1975. Other experiments of this type have shown an increase in microbial populations after contamination by oil, possibly due to an increase in nutrients and organic substrate as the oil is broken down.

Total streptomycetes show the same sharp increase after application of oil but they do not show as drastic a drop in the hot summer months. In the Spring of 1975 the streptomycete numbers had reached the level that they were in June 1974.

The total fungi numbers do not respond noticeably to the addition of oil. They remain approximately the same throughout the Summer, then begin to decrease, reaching the low point in November 1974 and throughout the winter to March 1975. The April and May 1975 samples again show an increase in numbers. This may be a result of cultivating the soil again, providing better aeration of the soil which the fungi need. It appears that fungi are not significant contributors to oil decomposition.

The anaerobic bacterial numbers do not show any response to the addition of oil. Their numbers change little until March 1975, when there is an increase. At this point, the investigators are not certain whether this increase is due to imperfect anaerobic conditions or to increased anaerobic conditions in the very moist, undisturbed winter soil. There is a decrease in the April samples, possibly because cultivation aerated the soil.

The hydrocarbon utilizers show the greatest response to the addition of the oil. Their numbers shot up to 10 per gram of soil. This also dropped sharply in the summer months as did the other groups. March 1975 again showed an increase in hydrocarbon utilizers.

The lipolytic organisms give the same results as hydrocarbon utilizers. There was a sharp increase after addition of oil, then a sharp drop which leveled off until November. March 1975 again showed a sharp increase in numbers.

The major microbial species found during the first vegetative season were Corynebacterium, Bacillus, Arthrobacter, Pseudomonas, Flavobacterium, Acinetobacter, 6

Alcaligenes, *Micrococcus*, and a yeast; *Proteus*, *Serratia*, and *Staphylococcus*, also appeared. In the second vegetative season so far we have generally observed a decrease in gram positive rods such as *Corynebacterium* and an increase in gram negative rods such as Acinetobacter. and *Alcaligenes* occurred. Yeast species also disappeared.

Oil on the fertilized plots had degraded approximately 80% by Fall 1975. On a study plot that had not been fertilized the oil had degraded only 55%. Since the oils were originally lubricating oils they were probably more complex chemically which could retard degradation rates.

The cultivated plots have been invaded by the wild sunflower at various degrees. Plots E and F, and L to N have limited invasion, whereas plot B has luxurious growth. Others are intermediate. The reasons for this variation has not been evaluated as yet.

FUTURE PLANS

The information available at this time on the degradation process is encouraging enough that further tilling or fertilizer additions are not expected. Future efforts will include continuing the technical monitoring of the site by Utah State University with some of the emphasis shifting to heavy metals uptake by the vegetation that grows on the plots.

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BEHAVIOR OF HIGH PESTICIDE CONCENTRATIONS IN SOIL WATER SYSTEMS

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ABSTRACT

Factors effecting pesticide mobility from hazardous waste disposal sites containing high pesticide concentrations were examined. Major consideration was given to the influence of the shape of the adsorption isotherm on pesticide mobility. Equilibrium adsorption of dimethylamine salt of 2,4-D [(2,4-Dichlorophenoxy) acetic acid] on Webster silty clay loam was measured in the concentration range of 0-5000 μg/ml. The adsorption isotherm was nonlinear in shape with the exponent in the Freundlich equation equal to 0.71. The adsorption sites for 2,4-D on the Webster soil were not saturated even in the presence of 5000 μg/ml of 2,4-D (amine salt). The mobility of 2,4-D in the Webster soil at various 2,4-D concentrations was simulated with a numerical solution to the solute transport model. These simulations revealed that pesticide mobility increased as solution concentration increased when $N < 1.0$. However, an increase in solution concentration resulted in a decreased mobility when $N > 1.0$. The pesticide solution concentration did not influence the mobility when $N=1.0$. Serious errors may be introduced by assuming a linear adsorption isotherm ($N=1$) when predicting pesticide transport under waste disposal sites where high pesticide concentrations exist. A procedure for estimating the arrival time of a selected pesticide concentration at various soil depths below a disposal site is presented and discussed.

Organic pesticides currently play an important role in food and fiber production in the United States. These materials have increased the efficiency of agricultural production as well as improved man's living conditions. In general, application concentrations for most agricultural, industrial, and domestic systems are low and do not pose a direct problem unless accumulated in the soil or biological systems. However, because of the volume of pesticides being produced and used, the problems associated with disposal of surplus and/or waste pesticide materials and empty or partially empty pesticide containers has become acute.

The soil as a sink for the disposal of pesticides has come under attack by environmentalists (1). Presently many unused pesticides and empty containers are buried in the soil (45 - 60 cm below the surface in sandy soils). This procedure does not guarantee that the chemical pesticide will remain at the disposal site. Therefore, the disposal site and the area around it may become contaminated and hazardous to human and animal health as well as plant and other biological systems.

Physical, chemical, and biological processes that influence the fate and behavior of specific pesticides present in the soil at low concentrations (0 - 10 μg/ml) have been studied extensively. However, the direct application of this information to soil-pesticide systems containing chemical concentrations several orders of magnitude higher have not been considered in detail. For example, the biological activity of previously viable soil micro-organisms may be reduced or stopped in the presence of a pesticide at waste or container concentrations. Also, pesticide movement through the soil and into the groundwater may be increased significantly owing to adsorption-desorption characteristics of a pesticide at high concentrations.

The application of existing pesticide-soil information to describe the mobility of pesticides from disposal sites containing high pesticide concentrations will be discussed in this manuscript. Adsorption-desorption characteristics for a pesticide and soil will be given major consideration. Also, a conceptual process-oriented approach to modeling pesticide behavior in soils will be presented.

THEORY

The mobility of a pesticide molecule in a soil-water system is directly influenced and controlled by the adsorption-desorption characteristics for the pesticide and soil. Several reviews describe in considerable detail mechanisms for pesticide adsorption by soils (2,3,4,5). In order to quantitatively describe the influence of adsorption on mobility, the adsorption-desorption characteristics must be described analytically. Numerous equations have been used to describe adsorption isotherms for pesticides (3,4). The Freundlich, Langmuir, and first-order kinetic equations are the most commonly used in the 0-10 μg/ml pesticide concentration range.

The Freundlich equation is purely empirical and may be stated as

$$S = KC^N \qquad [1]$$

where S is the amount of pesticide adsorbed per gram of soil (μg/g), C is the pesticide concentration in solution (μg/ml), and K and N are coefficients that vary with the chemical and soil. Equation [1] is valid only when equilibrium conditions exist between the adsorbed and solution phases. The empirical nature of the Freundlich equation is illustrated by the fact that a maximum adsorbed concentration is not reached as the solution concentration, C, increases without limit. However, the Freundlich equation has been successful for intermediate pesticide concentrations (3) where N was approximately unity.

A first-order kinetic adsorption equation has been used to describe adsorption in systems where soil-water flow exists (6). The kinetic adsorption equation may be written as:

$$\frac{\partial S}{\partial t} = k_D\left[\frac{k_A}{k_D}\frac{\theta}{\rho}C - S\right] \qquad [2]$$

where t is time (hr), k_A and k_D are forward and backward rate coefficients (hr^{-1}), θ is soil-water content fraction (cm^3/cm^3), ρ is soil bulk density (g/cm^3), and the other terms are the same as those described previously. Note that when $\partial S/\partial t=0$ (equilibrium) equation [2] reduces to equation [1] for $N=1.0$ and $K=k_A\theta/k_D\rho$. This approach is limited to the case where the equilibrium adsorption isotherm is linear and therefore may not be valid for systems with high pesticide concentrations.

The Langmuir equation is more conceptual in its description of adsorption and may be written as,

$$S = \frac{S_{max}\, b\, C}{1 + bC} \qquad [3]$$

where b is analogous to k_A/k_D (equation 2) and S_{max} is the maximum concentration that can be adsorbed by the soil. In general, the Langmuir equation has not been as successful as the Freundlich equation in describing pesticide adsorption in soil-water systems. The failure of the Langmuir equation is not surprising in that it assumes the energy for adsorption is constant and independent of surface coverage. Soils, because of their characteristic mixture of colloidal materials, do not have the same energy of adsorption over the entire surface area.

The movement of pesticides and other solutes through soils, under steady state soil-water flow conditions, have been described by the following partial differential equation (6,7,8,9):

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - V\frac{\partial C}{\partial x} - \frac{\rho}{\theta}\frac{\partial S}{\partial t} \qquad [4]$$

where D is the dispersion coefficient (cm^2/hr), V is the average pore-water velocity (cm/hr), (Darcy flux divided by soil-water content fraction), and the other terms are as described previously. The dispersion coefficient is a function of the average pore-water velocity (10). The first two terms on the right hand side of equation [4] describe the transport of the solute and the third term the adsorption-desorption of the solute. If the adsorption process is linear (equation 1 with N=1.0) equation [4] reduces to

$$R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - V \frac{\partial C}{\partial x} \qquad [5]$$

where,

$$R = 1 + \frac{\rho K}{\theta} \qquad [6]$$

and R is the retardation term (11). If the adsorption isotherm is nonlinear (N<1.0 or N >1.0), the retardation term is not a constant, but is dependent on the solution concentration as follows:

$$R = 1 + \frac{\rho K N C^{N-1}}{\theta} \qquad [7]$$

However, a weighted-mean value ($\bar{R}$) for the retardation term may be estimated (12),

$$\bar{R} = 1 + \frac{\rho K C_0^{N-1}}{\theta} \qquad [8]$$

where, C_0 is the maximum or incoming pesticide concentration (μg/ml). The influence of nonlinearity of the adsorption isotherm on pesticide mobility will be discussed later.

MATERIALS AND METHODS

The soil used in this study was obtained from the top 15 cm of a profile classified as Webster silty clay loam (Typic Haplaquoll). The soil profile is located in Boone County Iowa. The pH, organic matter content, and cation exchange capacity of the soil were 7.3, 3.87%, and 54.7 me/100g, respectively. The soil had 19%, 43%, and 39% sand, silt, and clay, respectively. The soil was air-dried and passed through a 2.0 mm sieve prior to storage and use.

Equilibrium adsorption of dimethylamine salt of 2,4-D [(2,4-dichlorophenoxy) acetic acid] on the Webster soil was measured using a batch experiment procedure. The 2,4-D solutions were prepared in 0.01 N $CaCl_2$ and spiked with 3.6 μCi/l of ^{14}C ring-labeled 2,4-D. Solution concentrations of 10, 50, 100, 500, 1000, and 5000 μg/ml were used for the adsorption study. A 5 g sample of the Webster soil and 10 ml of 2,4-D solution were equilibrated by shaking for 48 hrs. Following the equilibration, the samples were centrifuged at 800 x G for 30 min and the ^{14}C activity in the clear supernatent was determined by liquid scintillation. Triplicate samples were used for each concentration. The difference between initial herbicide concentration and the concentration in the supernatent was taken to be the amount of 2,4-D adsorbed by the soil. A mixture of antibiotics were added to all 2,4-D solutions to prevent the possibility of microbial degradation of 2,4-D during the 48 hr shaking period. The adsorption experiment was conducted at a constant temperature of 25 ± 0.5°C.

A numerical solution to equation [4] was used to simulate the mobility of 2,4-D at various concentrations in a Webster soil. The adsorption isotherm for 2,4-D and Webster soil was used to describe the adsorption-desorption process in equation [4].

RESULTS AND DISCUSSION

The adsorption isotherm for 2,4-D (dimethylamine salt) and Webster soil is presented in Figure 1. The data described by the Freundlich equation (equation 1) with K=4.34 and N=0.71. The fact that equation [1] describes the adsorption of 2,4-D over the concentration range studied (0-5,000 μg/ml) indicates that the adsorption sites were never saturated. This is not true for all 2,4-D adsorbent systems (13). The nonlinear relationship between the adsorbed and solution 2,4-D concentration phases has a direct influence on the mobility of 2,4-D in the Webster soil. Many studies have assumed and/or measured a linear relationship at low pesticide concentrations (14,15,16).

The significance of a nonlinear adsorption isotherm with regards to pesticide mobility was examined by simulating 2,4-D movement in the Webster soil with a numerical solution (9,17) of equation [4]. For the simulations, the values of ρ, θ, V, and D were assumed to be 1.4 g/cm^3, 0.3 cm^3/cm^3, 3.0 cm/hr, and 1.0 cm^2/hr, respectively. The values for K and N were taken from the experimentally measured isotherm unless stated otherwise (Figure 1). For the case considered in Figure 1, a pulse of 2,4-D with C_0=5000 μg/ml was introduced at the soil surface (x=0) for a period of 22 hrs, followed by an input of water with $C_0=0$ for an additional 48 hr period (total of 70 hrs).

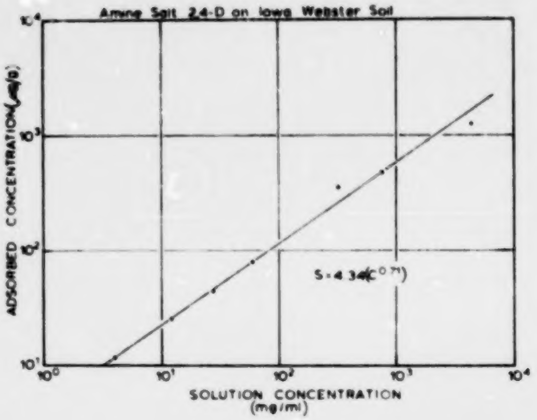

Figure 1. Adsorption isotherm for 2,4-D (amine salt) and Webster Silty clay loam.

Two simulated cases, $N=0.7$ and $N=1.0$, are presented in Figure 2. These illustrate that 2,4-D is less mobile at high concentration when $N=1.0$ than when $N=0.7$. The front of a nonreactive solute (eg. chloride) would be located at 210 cm for the above conditions (70 hr times the 3.0 cm/hr average pore-water velocity). The apparent difference in areas under the curves shown in Figure 2 is because more of the 2,4-D is in the adsorbed phase when $N=1.0$. The nonlinear isotherm $N<0.1$ also leads to an asymmetrical concentration distribution profile (Figure 2). The information presented in Figure 2 clearly points out the seriousness of assuming a linear isotherm to predice pesticide mobility under waste disposal sites where the pesticide concentrations may be high.

The mobility of a pesticide is also influenced by the magnitude of the solution concentration when the adsorption isotherm is nonlinear. Figure 3 presents the simulated 2,4-D concentration distributions in the Webster soil profile for two pesticide concentrations ($C_0=10$ and 5000 µg/ml. These curves were simulated using the same procedure as described above for Figure 2. The pesticide is much more mobile at high concentrations than at low concentrations.

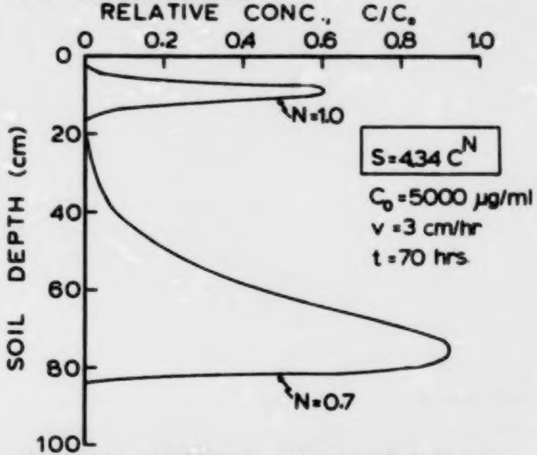

Figure 2. Simulated relative 2,4-D concentration distributions in the soil solution phase of Webster soil.

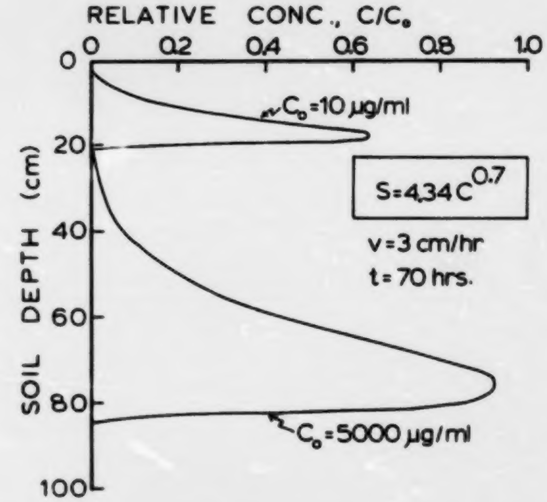

Figure 3. Simulated relative 2,4-D concentration distributions in the soil solution phase of Webster soil.

Both curves are asymmetrical in shape due to the nonlinearity ($N=0.7$) of the adsorption isotherm.

The dependence of pesticide mobility on the shape of the adsorption isotherm and solution concentration is summarized in Table 1. The retardation terms presented in Table 1 were calculated by using equation [8], with ρ=1.4 g/cm^3, and θ=0.3 cm^3/cm^3. A larger value for the retardation term represents a decreased mobility of the pesticide. The position of the pesticide front may be estimated by dividing the depth of water penetration (average pore-water velocity times input period) by the retardation term. It is apparent from the data presented in Table 1 that the pesticide mobility increases as C_o increases when N< 1.0. However, an increase in solution concentration results in decreased pesticide mobility when N > 1.0. The retardation terms are equal for all concentrations when N=1.0, and also equal for N values when C_o=1.0 µg/ml (Table 1). Thus, the error introduced by assuming linear adsorption isotherms may not be serious at low concentrations (< 10 µg/ml) but becomes significant at high pesticide concentrations.

TABLE 1. RETARDATION TERMS FOR VARIOUS PESTICIDE CONCENTRATIONS USING EQUATION [8] AND BULK DENSITY AND SOIL WATER CONTENT OF 1.4 g/cm^3 AND 0.3 cm^3/cm^3. RESPECTIVELY.

	C_o (µg/ml)				
N	1	10	100	1000	10,000
0.7	21.2	11.1	6.1	3.5	1.9
1.0	21.2	21.2	21.2	21.2	21.2
1.3	21.2	41.4	81.6	161.8	322.0

$S = 4.34\ C^N$

The pesticide transport model represented by equation [4] can also be utilized to predict the time required for a specific relative soil solution concentration (C/C_o) to be reached at any depth in the soil profile below a waste disposal site. The solution concentration entering the soil at the bottom of the waste disposal site is assumed to be constant and equal to C_o. Predicted relative concentrations (C/C_o) at selected depths for various reduced time (T/R) are shown in Figure 4. The C/C_o values are plotted on probability scale, while the values of T/R are plotted on a log scale. The reduced time scale can be converted to real time by multiplying the T/R values by the average retardation term ($\bar{R}$) for the soil-pesticide system in question (equation 8). The lines in Figure 4 were obtained under the assumption that a given amount of water passes through the disposal site (V is the average pore-velocity, m/yr). Graphs similar to Figure 4, but for different groundwater recharge rates can be generated with an analytical solution (11) to equation [4]. Graphs similar to Figure 4 may be of value in establishing site selection criteria.

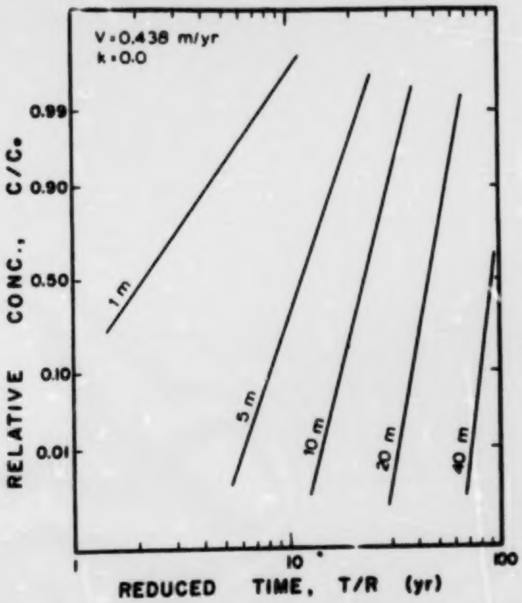

Figure 4. Simulated concentrations at various depths versus reduced time. The average pore-water velocity, V, times the average volumetric soil-water content fraction gives annual recharge rate.

Because most soil profiles are stratified in the vertical direction, considerable computer time is required to solve equation [4] for a soil profile with different soil-water and physical characteristics as well as solute adsorption properties in each layer. Numerical simulations of various multilayered soil profiles have shown, however, that the soil stratification sequence does not alter the shape or position of an effluent concentration distribution (17). Experimental results from the misicible displacement of ^{36}Cl and ^{14}C-labeled 2,4-D through a two-layered soil column supported the simulated results (17). Based on these results, it was concluded that effluent concentration distributions from multilayered soil profiles could be predicted by treating the soil as homogeneous or unstratified. The mathematical solution uses a weighted-mean retardation term based on the retardation terms for each layer in the profile. The procedure, however, can only be used for equilibrium linear and nonlinear adsorption processes.

SUMMARY

The shape of the adsorption isotherm plays a significant role in determining the mobility of adsorbed pesticides. This is especially important when considering high pesticide concentrations such as those found under a waste disposal site. Mobility studies conducted at low pesticide concentrations may not be of value for predicting the location of pesticides from a point source of high concentration. Pesticide mobility studies involving chemicals other than 2,4-D and soils representing five major soil orders in the United States are currently being conducted in our laboratory.

ACKNOWLEDGEMENTS

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THE MOBILITY OF THREE CYANIDE FORMS IN SOILS

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ABSTRACT

Three solutions of cyanide, KCN in de-ionized water (simple form), $K_3Fe(CN)_6$ in de-ionized water (complex form) and KCN in natural landfill leachate (mixed form) were each leached through five soils (Ava, Kalkaska, $Mohave_{Ca}$, Molokai, and Nicholson) of varying physical and chemical properties to evaluate which soil characteristics govern the movement of the various cyanide forms in soils. The effluent from each column was collected and analyzed for total cyanide each day. In general, KCN and $K_3Fe(CN)_6$ in water were both found to be very mobile in soils, while KCN in landfill leachate was found to be less mobile. Soil properties such as low pH, presence of free-iron oxide and kaolin, chlorite and gibbsite-type clay (high positive charges) tended to increase attenuation of cyanide in the three forms. High pH, presence of free $CaCO_3$ (high negative charges), low clay content and montmorillonite clay tended to increase the mobility of the three cyanide forms.

INTRODUCTION

Man's new sensitivity toward nature has caused him to seek new answers about the environment which surrounds him. Presently a busy area of research is the study of toxic compounds in soils. Cyanide is one of the compounds in question.

Cyanide is introduced into the soil by natural means and through the activities of man. It is produced naturally by several fungi (Bach, 1956), at least one bacterium (Michael and Corpe, 1965), and many members of the higher plant community (Robinson, 1962). The amount produced by these organisms is rather insignificant when compared to the quantity which is discarded each day as a waste product of some modern industries. Cyanide has been used extensively since the 1800's for extracting precious metals and for stripping undesirable foreign substances from metal surface before plating. Cyanide is introduced into the waste system by drag-out losses, leakage and accidental tank spills. Rudolph (1953) estimated cyanide concentration of the $CN^{\ominus}$ in the waste stream of cyanide plants varied from 100 mg/l to 50,000 mg/l, depending on the efficiency of the plant and the process involved.

The highly toxic nature of the cyanide ion has been well documented. Ludzach (1951) and Schant (1939) found that it has an inhibitory effect on fish life at a concentration as low as 0.3 ppm. The U.S. Public Health Service (1961) suggested 0.01 mg of HCN/l to be the limiting concentration of cyanide in drinking water. These figures indicate the harmful effect that uncontrolled dumping of cyanide waste could have on aquatic life and human health. Fortunately, cyanide waste is treated in most plants. Methods range from chemical treatment (alkaline chlorination, acidification, ponding, complexation, ozonation and electrolytic oxidation) to biological treatment using activated sludge (Murphy and Nesbitt, 1964). Although some of these processes (alkaline chlorination and activated sludge) are quite effective, none of them completely remove the cyanide.

Due to the highly toxic nature of cyanide, it is important to gather information on its behavior in soils. The object of this investigation was to measure cyanide mobility in soils and to determine which soil properties govern the mobility and/or attenuation of cyanide in soil.

MATERIALS AND METHODS

Three solutions of cyanide (Table 1), KCN in de-ionized water (simple form), $K_3Fe(CN)_6$ in de-ionized water (complex form) and KCN in natural landfill leachate (mixed form) were each leached through five soils (Ava silty clay loam, Kalkaska sand, Mohave_{Ca} clay loam, Molokai clay and Nicholson silty clay). Table 2 shows some of the soil characteristics.

Taras (1971) defines the simple and complex form of cyanide as follows:

Simple form

$$A(CN)_x$$

where A = an alkali (Na, K, NH_4) or other metallic cations

x = the valence of A and the number of CN groups

CN is present as $CN^{\ominus}$ in solution

Complex form (Alkali-metallic cyanide)

$$A_yM(CN)_x$$

where A = the alkali present y times

M = the heavy metal (Fe^{3+}, Fe^{2+} and others)

x = the number of $CN^{\ominus}$ groups which is equal to the valence of A taken y times plus that of the heavy metal.

The anion radical in the complex form appears as $M(CN)_x^{\ominus}$.

TABLE 1. CHARACTERISTIC OF CYANIDE SOLUTION

Cyanide Solution	pH of Solution	Concentration of Cyanide in Solution	Type of Ion Present
		ppm	
KCN in de-ionized water	10.0	∿ 97	$CN^{\ominus}$
$K_3Fe(CN)_6$ in de-ionized water	8.5	∿ 98	$Fe(CN)_6^{\ominus}$
KCN in landfill leachate	7.0	∿ 80	Unknown

TABLE 2. CHARACTERISTICS OF SOILS

Soil	Order	pH	CEC	EC	Surface Area	Free Iron Oxide	Bulk Density	Sand	Silt	Clay	Texture Class	Predominant Clay Mineral
			meq/ 100g	µmhos/ cm	m^2/g	%	cm^3/g	%	%	%		
Ava (Illinois)	Alfisol	4.4	19	207	61.5	4	1.36	6	67	27	Silty Clay Loam	Vermiculite Kaolinite
Kalkaska (Michigan)	Spodosol	4.6	10	75	8.9	1.8	1.5	95	3	2	Sand	Chlorite Kaolinite
Molokai (Hawaii)	Oxisol	6.2	14	1262	67.3	23	1.33	23	25	52	Clay	Kaolinite Gibbsite
Nicholson (Kentucky)	Alfisol	6.7	37	176	120.5	5.6	1.34	3	47	49	Silty Clay	Vermiculite
Mohave$_{Ca}$ (Arizona)	Aridisol	7.8	12	510	127.5	2.5	1.53	32	28	40	Clay Loam	Mica Montmorillonite

The mixed material contains both the simple and complex forms. The formation of blue precipitate occurred when KCN was added to the leachate. Tests indicated the precipitate to be Prussian blue ($[Fe(CN)_6]_3Fe_4$). Other compounds of cyanide are present, but their actual identity is unknown.

The natural municipal solid waste leachate was produced by packing representative solid waste in a 3800 l commercial septic tank, saturating it with water and letting it digest for several months. Concentration levels of some constituents in the leachate appear in Table 3.

TABLE 3. ANALYSIS OF THE NATURAL LEACHATE FROM A MUNICIPAL WASTE-TYPE LANDFILL USED IN THIS STUDY

pH	6.7
EC (μmhos/cm)	2500
K (ppm)	240
Na (ppm)	60
Ca (ppm)	160
Mg (ppm)	33
Zn (ppm)	.3
Si (ppm)	14
Cl (ppm)	200
Fe (ppm)	90
Mn (ppm)	1.3

Miller (1906) reported carbon dioxide tended to degrade cyanide. Therefore, the leachate was aerated and the deionized water was boiled to drive off the dissolved CO_2.

The soils used were collected from the B and/or C horizons, dried in air and passed through a 2 mm sieve. Each soil was packed in a PVC column 5 cm in diameter and 10 cm long to a specified bulk density greater than natural conditions to avoid column side effects and insure uniform flow throughout.

The soils were saturated in an inverted position to provide uniform wetting and to exclude air. The cyanide solutions were pumped through the soil using a Pharmacia (Piscataway, NJ) Paristaltic pump. The flow rate was regulated to deliver approximately one pore volume of effluent per day. The effluent was collected in 125 ml plastic bottles containing 5 ml of 1 N NaOH. Sodium hydroxide stabilizes any cyanide coming through the column. The eluate was analyzed for total cyanide each day by the Liebig distillation method (Taras, 1971). Distillation of the sample is required to convert all the cyanide forms in the sample to simple cyanide (NaCN) which can be easily analyzed by the Liebig distillation method using silver nitrate and Rhodanine indicator (Taras, 1971).

RESULTS AND DISCUSSION

The relative mobility of the three cyanide solutions is best illustrated in $Mohave_{Ca}$ clay loam and Kalkaska sand (Figures 1 and 2). All data are plotted as pore volume versus C/C_{max}, where C/C_{max} is the ratio of effluent concentration to influent concentration. KCN and $K_3Fe(CN)_6$ in de-ionized water were both found to be very mobile in soils, while KCN in landfill leachate was the least mobile of the three solutions.

The effect of soil type on the movement of the three cyanide solutions is illustrated in Figures 3, 4, and 5. Figure 3 shows the amount of KCN in de-ionized water that was leached through four soils, $Mohave_{Ca}$, Ava, Nicholson, and Molokai. The figure indicates KCN leached most rapidly in the soil having the highest pH and free $CaCO_3$ ($Mohave_{Ca}$ clay loam). The negative charges on the clay surface of $Mohave_{Ca}$ tends to repel the $CN^{\ominus}$, causing it to be leached out more rapidly than in acid soils. The $CN^{\ominus}$ was retained most by soils having a high concentration of Mn and hydrous oxides of Fe (Nicholson silty clay and Molokai clay). Korte et al. (1975) found similar results working with the anion forms of As, Cr, Se, and V. This conclusion is further supported by data from Berg and Thomas (1959). They found $Cl^{\ominus}$, which is similar to $CN^{\ominus}$ in its

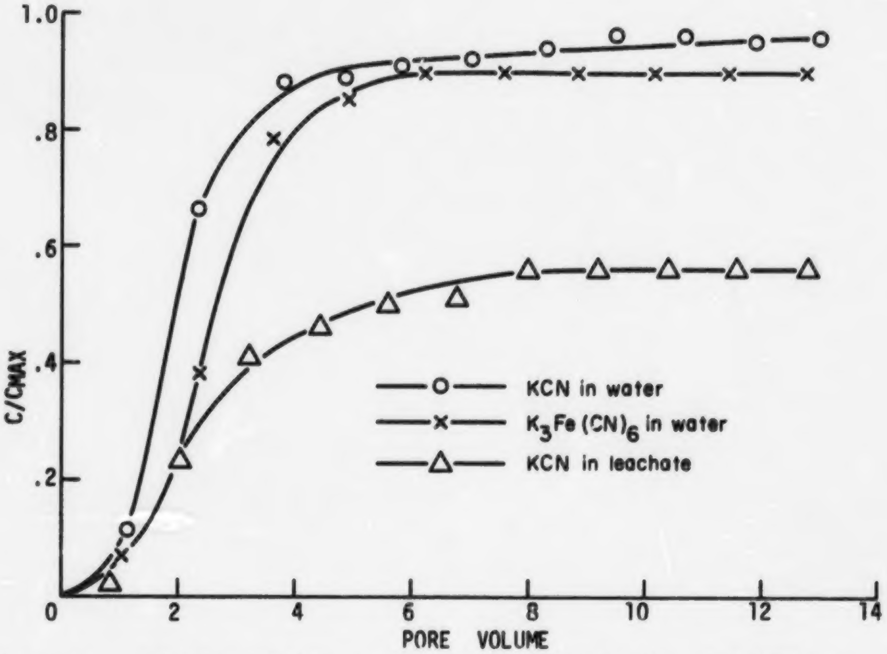

Figure 1. Relative mobility of KCN in de-ionized water, $K_3Fe(CN)_6$ in deionized water and KCN in leachate through Kalkaska sand.

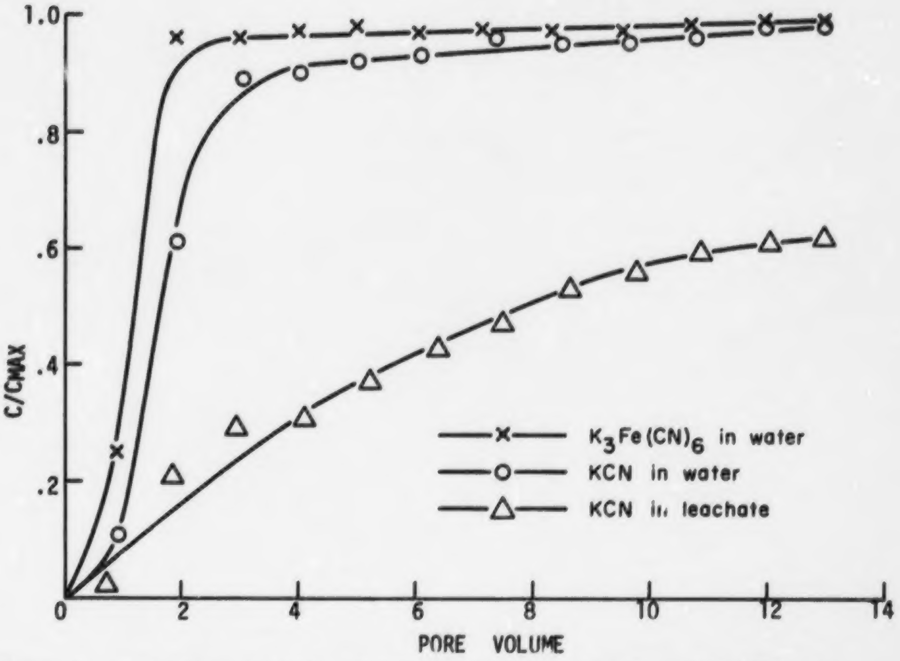

Figure 2. Relative mobility of KCN in de-ionized water, $K_3Fe(CN)_6$ in de-ionized water and in leachate through Mohave_{Ca} clay loam.

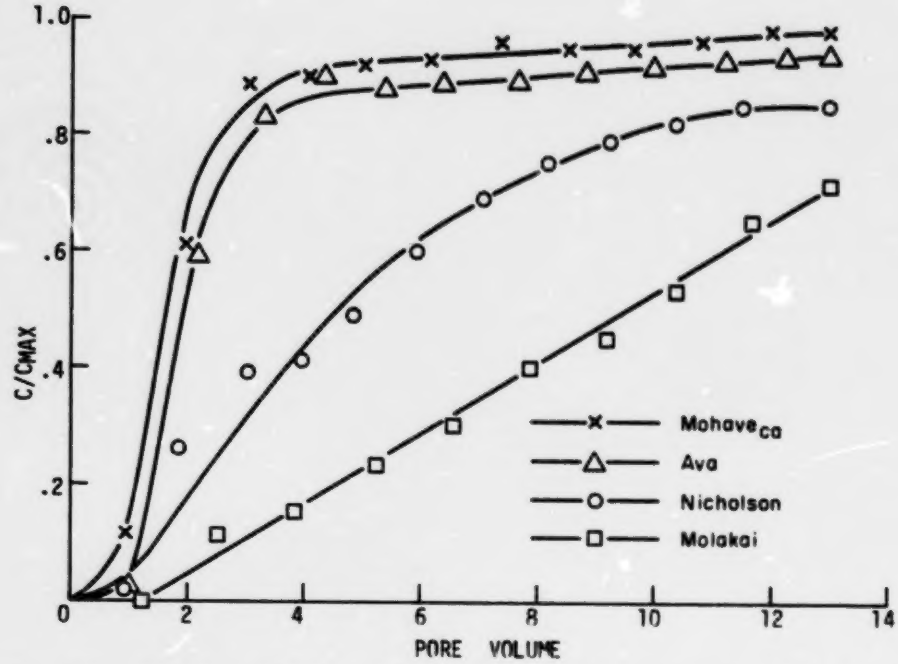

Figure 3. Relative mobility of KCN in de-ionized water through four diverse soils.

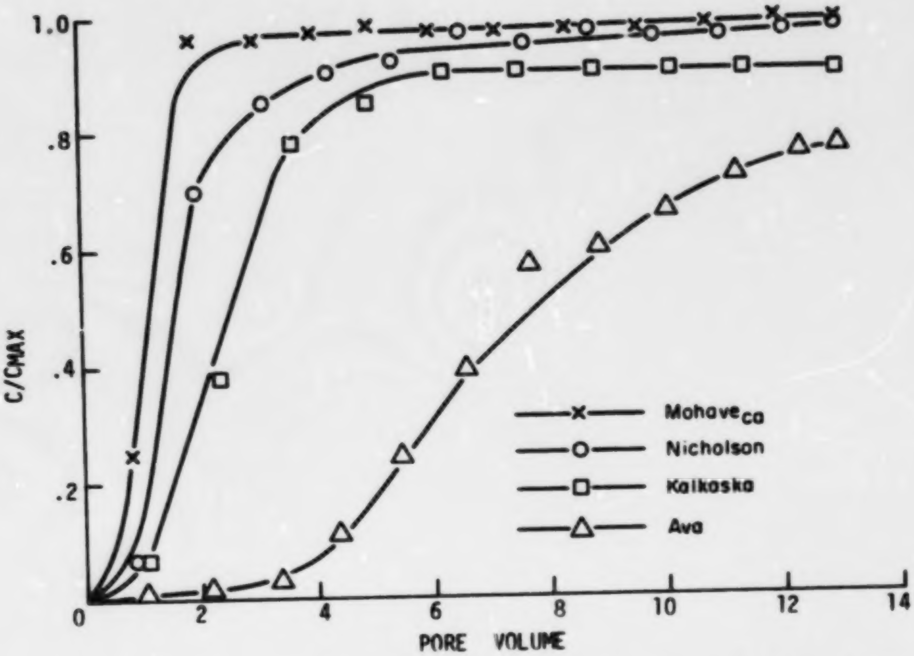

Figure 4. Relative mobility of $K_3Fe(CN)_6$ in de-ionized water through four diverse soils.

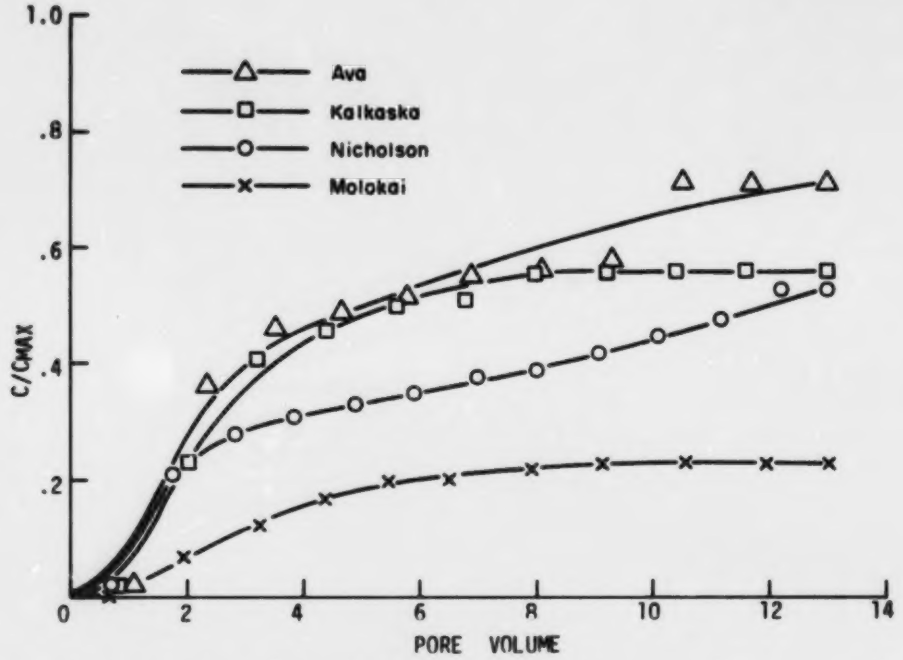

Figure 5. Relative mobility of KCN in leachate through four diverse soils.

adsorption behavior, attenuated in soils having a high percentage of kaolin clay and iron and aluminum oxides. Schofield (1939) also reports that soils high in these oxides have a high anion exchange capacity. Kamprath (1956) found good retention of SO_4^{2-} by an acidic soil high in oxides and kaolin, whereas the 3-layer minerals appeared to have poor retention for SO_4^{2-}. The acidic soil (Ava silty clay loam) in this study proved on the contrary, to be a poor attenuator of $CN^{\ominus}$. Texture seems to have little measurable effect on the attenuation of KCN. Free iron oxide and $CaCO_3$ seem to have a greater influence on the movement of KCN in water than either soil pH or texture.

Figure 4 illustrates the movement of $K_3Fe(CN)_6$ in de-ionized water through four soils (Mohave$_{Ca}$ clay loam, Ava silty clay loam, Nicholson silty clay loam and Kalkaska sandy loam). The ferricyanide ion also migrated most rapidly through soils having a high pH and in the presence of free $CaCO_3$ (Mohave$_{Ca}$ clay loam) for the same reason as KCN in water. Ferricyanide moved slowest in soils having a low pH (Ava silty clay loam and Kalkaska sandy loam). A low pH would indicate the clay surface to have a high percentage of positive exchange sites which would attract the $Fe(CN)_6^{3-}$ ion and retain it. Texture seems to play a more important role in this case. The high clay content soil (Ava silty clay loam) retained more of the $Fe(CN)_6^{3-}$ than the sandier soil of similar pH (Kalkaska sandy loam). Although iron-oxide seemed to have some affinity for $Fe(CN)_6^{3-}$, its presence was not as effective as soil pH in governing the movement of this form of cyanide.

Figure 5 portrays KCN in landfill leachates migrating through four soils (Ava silty clay loam, Kalkaska sandy loam, Nicholson silty clay and Molokai clay). This solution moved most rapidly through soils with low pH (Ava silty clay loam and Kalkaska sandy loam). Cyanide was retained most by soils having a high concentration of iron-oxide. Cyanide in leachate seemed to behave similarly to KCN in de-ionized water.

Of the three solutions, KCN in leachate was found to be attenuated the best. This can be partly explained by the precipitation of Prussian blue when KCN was added to the leachate (Robine, Lenglen and LeClere, 1906). This blue precipitate was found permeating the top 4 cm of the soil columns. The accumulation indicates that Prussian blue may be quite immobile in soils. The cyanide that came through the soil probably was the $CN^{\ominus}$ that did not react with the Fe in solution to form Prussian blue.

The anaerobic state of the soil columns inhibited any microbial degradation of cyanide. Micro-organisms responsible for degrading cyanide under anaerobic conditions are very sensitive to high cyanide concentration. Coburn (1949) found 2 ppm in the wastestream to be the limit for effective anaerobic degradation of cyanide. This concentration is much less than that passed through the soil columns.

CONCLUSION

Cyanide as $Fe(CN)_6^{3-}$ and $CN^{\ominus}$ in water were found to be very mobile in soils. Cyanide as KCN in natural landfill leachate was found to be less mobile. Soil properties such as low pH, percent free-iron oxide and kaolin, chlorite and gibbsite type clay (high positive charges), tended to increase attenuation of cyanide in the three forms. High pH, presence of free $CaCO_3$ (high negative charges), low clay content and montmorillonite clay tended to increase the mobility of the cyanide forms. Cyanide could possibly contaminate the groundwater if proper treatments are not used.

ACKNOWLEDGMENT

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CONTAMINANT ATTENUATION - DISPERSED SOIL STUDIES

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ABSTRACT

Traditionally the approach to the examination of contaminant interaction with soil has involved soil column experimentation. This paper presents the results of a study evaluating the attentuation of two liquid industrial wastes in soils typical of the Ontario environment using a dispersed soil methodology which was shown to be suitable for use to approximate the behavior of contaminants in soil. The liquid industrial wastes, supplied by the Ontario Ministry of the Environment, were two steel plant wastes - Stretford Liquor and Alkaline Cleansing Liquid Waste. Subsequent to characterization of the soil and the liquid industrial waste, the attenuation of the liquid waste in the soil was examined in a sorption and desorption phase. In the sorption phase the amount of contaminants attenuated were calculated while the amount and extent of contaminant release was calculated in the desorption phase. The results of the dispersed soil studies were used as input to a Soil-Waste Interaction Matrix for environmental assessment and as a design tool to project contaminant concentrations in a simplified hydrogeologic environment under a given geometry of liquid waste application to the soil.

INTRODUCTION

Environmental legislation in Canada currently limits the discharge of solid or liquid industrial waste to the land to those sites where it has been demonstrated that a minimal environmental impact will be effected. Historically, the soil has proven to be an acceptable waste recepticle. Environmental impact resulting from the discharge of leachate from a solid waste or from the infiltration of a liquid waste into soils at a disposal site has to date generally been of an aesthetic nature rather than one of receiving water quality degradation. The capacity of the soil to attenuate contaminants by the physical, chemical and biological processes described by mechanical filtration, precipitation and co-precipitation, sorption, gaseous exchange, diffusion and dispersion, and microbial activity, is held to have controlled contaminant migration to within acceptable distances.

However, the scientific technology to assess or predict the attenuation capacity of a soil is only now being developed. Environmentalists argue that this information is needed in order to adequately assess the environmental suitability of a waste disposal system.

Contaminant interaction with soil has been studied in many research programmes (1, 2,3,4). These were intended to provide input data for the modelling of contaminant migration in soil. The U.S. Environmental Protection Agency intends that the input data be collected using a standard procedure for the evaluation of the soils contaminant attenuation capacity (5).

Recognizing the need to develop a methodology for assessing an industrial waste disposal site suitability, relative to other proposed sites, the Solid Waste Management Branch of Environment Canada has also been working towards the development of a standard environmental assessment procedure, for the use by provincial pollution control agencies. The procedure now being finalized would enable regulatory agencies to evaluate a number of alternate waste disposal sites based on a simple, yet comprehensive, waste-soil site rating scheme. The procedure will involve the use of soil-waste interaction matrices for the purpose of rating proposed sites for environmental acceptability based on a number of criteria, and for the purpose of predicting the attenuation and mobility of industrial wastes in soils.

The examination of contaminant interaction with the soil has been studied by Farquhar and Rovers (1) using a dispersed soil methodology. The research showed "that the dispersed soil experiments can be used to approximate the behavior of contaminants in soil" when flow conditions in the field would be intergranular. The use of a dispersed soil model wherein an instantaneous well mixed condition exists also has been found to be suitable for use in mathematical modelling (6).

The purpose of this paper is threefold. Firstly, the paper describes the development of a standard environmental assessment procedure suitable for alternate waste disposal site evaluation. Secondly, the paper describes the attenuation and desorption characteristics of two liquid industrial wastes, Stretford liquor and alkaline cleansing waste, on three soils typical of the Ontario environment. Thirdly, the paper describes the use of the attenuation and desorption data as input to a standard environmental assessment procedure and the use of the data in design to evaluate the zone of influence of a liquid waste disposal on land system.

ENVIRONMENTAL ASSESSMENT PROCEDURE

Soil-Waste Interaction Matrix Procedure (SWIMP)

The environmental assessment procedure being developed has been named the SOIL-WASTE INTERACTION MATRIX PROCEDURE (SWIMP).

A site dependent matrix is being constructed using columns of soil-site parameters and rows of waste characterization parameters. The basic structure of the matrix is depicted in Figure 1.

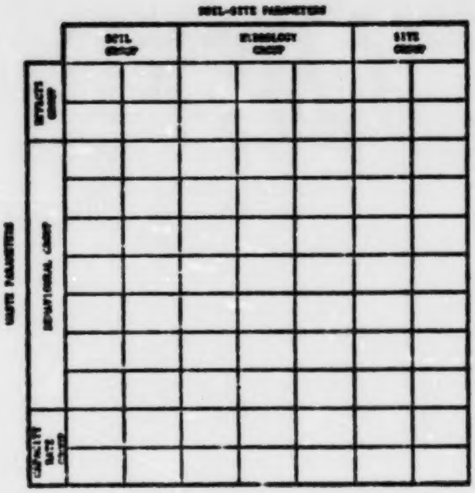

FIGURE 1. SOIL-WASTE INTERACTION MATRIX (SITE DEPENDENT)

This matrix may be used as follows. Matrix inputs are generated by determining parameter values, for a given waste and a given site, in points or arbitrary units. These values are entered into the matrix as shown in Figure 2. Waste parameter values are combined with soil-site parameters to provide matrix interaction elements. The sum of the matrix elements may be used to provide an overall point score for comparison either with other point scores, or with a scale of arbitrary acceptability.

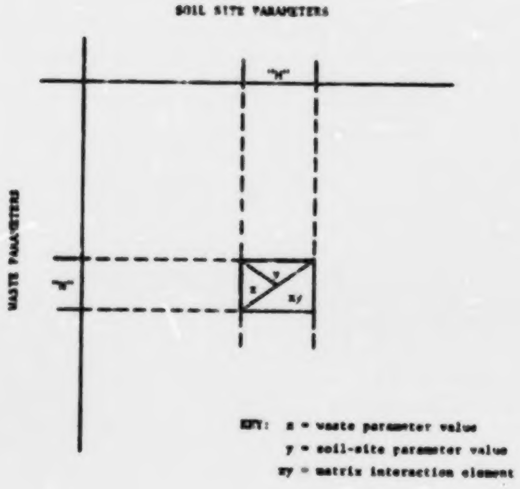
SOIL SITE PARAMETERS
"N"
WASTE PARAMETERS
"M"
y
x
xy
KEY: x = waste parameter value
y = soil-site parameter value
xy = matrix interaction element

FIGURE 2. SWIMP (SOIL-WASTE INTERACTION MATRIX PROCEDURE)

As a sub-set of this site dependent matrix, a site independent matrix is also being developed. This matrix consists of columns of soil types and rows of waste composition parameters. A matrix entry is essentially a soil attenuation factor, as shown in Figure 3.

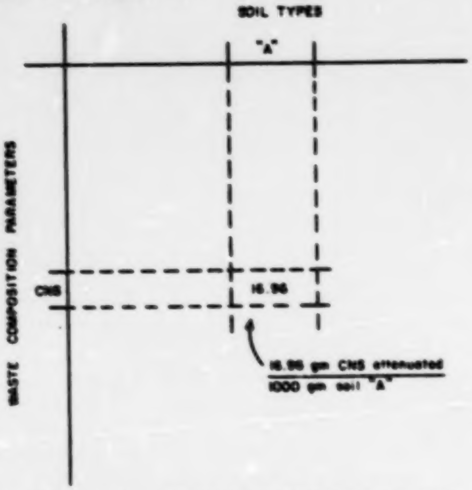
SOIL TYPES
"A"
WASTE COMPOSITION PARAMETERS
CNS
16.96
16.96 gm CNS attenuated
1000 gm soil "A"

Figure 3. SITE INDEPENDENT MATRIX

Matrix entries are attainable from past or current soil-waste interaction studies, or possibly from field data which is being collected routinely by pollution control agencies. In time, the matrix may become entirely filled using results from dispersed soil study techniques such as have been developed by Farquhar and Rovers (1).

The attenuation information which is intended to be input into the site dependent matrix can be used in two ways. First of all, the information can be used to calculate an attenuation parameter value as an input to the site dependent matrix. Once the best site is chosen, the information from dispersed soil studies can be reworked, as will be discussed later, to assist in site design and contaminant migration modelling for the chosen site.

DISPERSED SOIL STUDIES

Methodology

The dispersed soil methodology used to investigate the contaminant interaction of the liquid waste, Stretford liquor and alkaline cleansing waste, with soil has previously been detailed (1). The development and evaluation of the dispersed soil methodology was done in experiments employing sanitary landfill leachate.

For each industrial waste 3 sets of 5 reactors, one for each of the 3 soils used, were placed in series and prepared by placing 200 gm of air dry soil in the reactor, bringing the soils to "field capacity" through the addition of groundwater, purging the reactor with nitrogen and sealing from the environment.

In the sequence of 5 reactors per soil, 200 ml of industrial liquid waste was added to the first reactor and mixed. The liquid after chemical equilibrium in the reactor had been reached was then drained from the soil which was then passed on to the next of the 5 reactors in series. An aliquot of the filtrate was taken for chemical analysis following drainage from the first, third and last reactor.

Subsequently a total of 5 slugs, each of 200 ml volume, of groundwater was passed through the 5 reactor series to evaluate the desorption of contaminants attenuated.

Figure 4 schematically presents the dispersed soil study model.

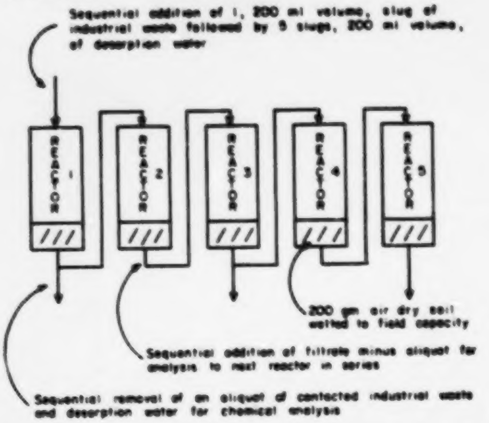
Sequential addition of 1, 200 ml volume, slug of industrial waste followed by 5 slugs, 200 ml volume, of desorption water
REACTOR 1
REACTOR 2
REACTOR 3
REACTOR 4
REACTOR 5
200 gm air dry soil wetted to field capacity
Sequential addition of filtrate minus aliquot for analysis to next reactor in series
Sequential removal of an aliquot of contacted industrial waste and desorption water for chemical analysis

Figure 4. SCHEMATIC OF DISPERSED SOIL STUDY MODEL

Table 1 shows the sequence of experimental activities per single soil per single industrial waste.

TABLE 1. SEQUENCE OF EXPERIMENTAL ACTIVITIES

Sequential Activities	Sorption Slug	Desorption Slug Number				
		1	2	3	4	5
1	R1#	-	-	-	-	-
2	R2	R1*	-	-	-	-
3	R3#	R2	R1+	-	-	-
4	R4	R3*	R2	R1+	-	-
5	R5#	R4	R3+	R2	R1+	-
6	-	R5*	R4	R3+	R2	R1+
7	-	-	R5+	R4	R3+	R2
8	-	-	-	R5+	R4	R3+
9	-	-	-	-	R5+	R4
10	-	-	-	-	-	R5+
11	-	-	-	-	-	-

R1 denotes reactor 1.
#detailed chemical analysis of post-contact liquid waste
*detailed chemical analysis of post-contact desorption liquid
+partial chemical analysis of post-contact desorption liquid

Experimental Materials

Soil

Three soils, selected to exhibit a typical range of fine grained soils representative of Southern Ontario, were contacted with the industrial liquid waste. The soils range was selective to fine grained ice-contact soils deposited by the last period of glaciation in Southern Ontario. Present knowledge indicates that fine-grained soils are best suited for liquid waste disposal.

The soil characteristics prior to contact with the liquid waste are presented in Tables 2 and 3. Table 2 presents the grain size, cation exchange capacity and moisture content of the soils while Table 3 presents the mineralogical character of the soil.

Industrial Waste

Two industrial liquid wastes from a steel plant, Stretford liquor and alkaline cleansing wastes, were contacted with the three soils. Table 4 presents the quality characteristics of the liquid waste considered to be of most concern and given primary consideration in the sorption and desportion studies.

TABLE 2. SOIL CHARACTERIZATION-CHEMICAL AND PHYSICAL

Soil Character / Soil	Soil 1	Soil 2	Soil 3
Grain Size-Clay	4%	10%	28%
-Silt	65%	59%	66%
-Sand	31%	31%	6%
Soil Type	Silty Loam	Silty Loam	Silty Clay Loam
Cation Exchange Capacity meq/100 gm	2.27	3.89	10.52
Moisture Content	8.04%	7.1%	19.01%

TABLE 3. SOIL MINEROLOGY

	MICA	VERMICULITE	CHLORITE	CHLORITE	MONTMORILLONITE	CHLORITE	MONTMORILLONITE	KAOLINITE	FELDSPAR	QUARTZ	AMPHIBOLE	VERMICULITE
Soil 1	X	L		X	ND		ND	X	ND	L	ND	ND
Soil 2	X	X		X	ND		ND	X	ND	L	ND	ND
Soil 3	X	X		X	ND		ND	X	ND	L	ND	ND

X - dominant; L - present; ND - not detected

DATA ANALYSIS AND INTERPRETATION

Calculation

The chemical data describing the changes in contaminant concentration during the migration of the liquid waste and desportion water through the dispersed soil reactors were used to calculate:

1. the net attenuation of each contaminant by all processes including dilution.
2. the net attentuation minus the effect of dilution for each contaminant, and
3. the net desorption for each contaminant.

The liquid waste and desorption water upon being mixed with the moist sample is diluted initially by the soil moisture. In the field situation diffusion and dispersion would result in a similar effect being imparted on the migrating contaminant. However the magnitude of the effect

TABLE 4. CHEMICAL PARAMETERS STUDIED IN DEPTH IN THE LIQUID WASTE

STRETFORD LIQUOR	
*total solids	288,000 mg/l
chemical oxygen demand (COD)	15,000 mg/l
*total organic carbon (TOC)	28,800 mg/l
*thiosulphate (S_2O_3)	36,750 mg/l
*thiocyanide (CNS)	140,500 mg/l
*sulphate (SO_4)	12,818 mg/l
*sodium (Na)	86,000 mg/l
*total iron (Fe)	84 mg/l
*vanadium (V)	90 mg/l
*lead (Pb)	3.2 mg/l
*Cadmium (Cd)	.460 mg/l
ALKALINE CLEANSING WASTE	
*total solids	50,000 mg/l
chemical oxygen demand (COD)	6,500 mg/l
*total organic carbon (TOC)	3,800 mg/l
*total phosphorus (P)	720 mg/l
*sulphate (SO_4)	19,135 mg/l
*pH	13.1
*total iron (Fe)	520 mg/l
*total manganese (Mn)	46 mg/l
*sodium (Na)	24,000 mg/l
*Aluminum (Al)	13.00 mg/l

*Characteristics given primary consideration in the sorption and desorption studies.

would be less. Therefore the dispersed soil data would be corrected to account for this difference. This is discussed further on in the report. Therefore, in this paper the field mechanism of diffusion and dispersion is related to the mechanism of dilution effected in the dispersed soil test. In both cases the effect is to decrease the contaminant concentration.

The calculation of the net attenuation of a contaminant at each point in the dispersed soil reactor series was calculated as

$$A_{N,D} = \frac{\left(\frac{M_T - M_E}{M_T}\right)(M_I)}{W_S} \qquad (1)$$

where

$A_{N,D}$ = net attentuation including dilution - mg contaminant per gm soil
M_T = mass of contaminant having potential as effluent - mg
M_E = mass of contaminant in effluent - mg
M_I = mass of contaminant in influent-mg
W_S = dry weight of soil - gms

where

$$M_T = \frac{(V_I x C_I)+(V_D x C_D)+(V_S x C_S)(1.0-f_E)}{1000}$$

$$M_E = \frac{(V_E \times C_E)}{1000}$$

$$M_I = \frac{(V_E \times C_I)}{1000}$$

where

V_I = volume of influent liquid waste - mls
V_D = volume of soil water exiting as effluent - mls
V_E = volume of effluent - mls
C_I = concentration of contaminant in influent liquid waste - mg/l
C_S = concentration of contaminant in soil water - mg/l
V_S = volume of soil water at field capacity - mls
f_E = correction factor
C_D = concentration of contaminant in soil water exiting as effluent-mls
C_E = concentration of contaminant in effluent - mg/l

The purpose and development of the empirical correction factor, f_E, is discussed subsequently.

The calculation of attenuation not including dilution for a contaminant under consideration at each point in the dispersed soil reactor series was given by:

$$A_N = \frac{\left(\frac{M_T - M_E - M_S}{M_T}\right) M_I}{W_S} \qquad (2)$$

where

A_N = attenuation not including dilution - mg contaminant per gm soil
M_S = mass of contaminant in soil water - mg

$$M_S = \frac{C_E \times V_S \times f_E}{1000}$$

The data were also to be presented in

graphical form as C/C_o versus S_M/V_{LW} or S_M/V_{DW} with dilution included where:

C = concentration of contaminant after contact with soil in batch reactor - mg/l

C_o = initial concentration of contaminant in liquid waste influent - mg/l

$\frac{S_M}{V_{LW}}$ = gms soil per ml liquid waste

$\frac{S_M}{V_{DW}}$ = gms soil per ml desorbing water.

The dispersed soil reactors permit the complete intermixing of the soil water and the influent liquid waste. Therefore for a known volume of liquid waste and soil and a measured moisture content of the soil the diluted concentration of an influent contaminant can be calculated from the dispersed soil reactor. This was given by:

$$C_E = \frac{V_I C_I + V_S C_S}{V_I + V_S}$$

In a field situation where a volume of liquid waste is allowed to contact a certain mass of soil the average effluent concentration of the leachate would be calculated somewhat differently. Dispersion and diffusion in the field (or undisturbed column) differs from that of the dilution provided in the dispersed soil reactors(1). In the field situation, "dilution" is provided by the effective moisture content where the volume of liquid waste being "diluted" equals the effective pore space, ρE, in an incremental soil volume. This represents a mixing ratio. In effect the liquid waste is routed through the soil volume with the average effluent contaminant concentration given by:

$$C_E = [\frac{V_{I,1} \times C_I + V_{S,E} \times C_{S,o}}{V_{I,1} + V_{S,E}} + \frac{V_{I,Z} \times C_I + V_{S,E} \times C_{S,1}}{} + \ldots \frac{V_{I,N} \times C_I + V_{S,E} \times C_{S,N-1}}{V_{I,N} + V_S}] + \frac{1}{\frac{V_I}{\rho E}}$$

where

$V_{I,N}$ = volume of influent liquid waste - ml
= $\rho S_V - V_S$
ρ = porosity
S_V = volume of soil - cc
$C_{S,A-1}$ = concentration of contaminant in soil water volume preceding the addition of $V_{I,N}$ - mg/l
$V_{S,E}$ = soil water volume available as dilution water - mls
ρE = effective porosity or pore space
= $\rho S_V - V_S$

It has been shown that the predicted breakthrough curve differs from the observed breakthrough curve for chloride (Cl)(1). The predicted breakthrough curve is calculated on the assumption that the total volume of soil water is available for "dilution" of the contaminant concentration while in fact this is not the case in the field or an undisturbed column. Therefore, the predicted attenuation is greater than that measured.

In the dispersed soil reactors all of the soil water volume acts to dilute the contaminant concentration. Therefore, the effluent contaminant concentration measured in the batch reactor is less than that which would be measured in the field.

In order that the changes in the liquid waste chemistry can be related to a field situation, an empirical correction factor, f_E, must be used. This factor corrects the contaminant concentration measured by the dispersed soil technique to correspond to the field situation or an undisturbed soil column where the diluting mechanism is diffusion-dispersion.

It accounts for two (2) conditions: (1) that, in the dispersed soil reactor, the liquid waste and the soil water are not mixed in the proportions existing in the field and (2) that the intermixing of constituents between the liquid waste and the soil water, while virtually complete in the dispersed soil reactor, may not be so in the field.

To this point in time it has not been possible to predict values for f_E. For this research then, it was necessary to make use of existing experimental data collected under varying conditions (1) to determine values of f_g.

The value of f_g equal to .71 was used for this study.

Data Presentation

For purposes of this paper the data analysis and discussion will be limited to the interaction of the Stretford liquor with the 3 soils. The contaminants considered included total organic carbon (TOC), thiosulphate (S_2O_3), thiocyanide (CNS), sodium (Na), total iron (Fe), vanadium (V), lead (Pb), cadmium (Cd) and chloride (Cl).

Contaminant Attenuation

Tables 5, 6 and 7 summarizes the attenuation and desorption data in the three soils for the contaminants described above. The tables show the influence of "dilution" as a means of attenuation, the principles of which were set out earlier. The influence was felt for all contaminants but was clearly the major attenuation mechanism for thiosulphate (S_2O_3), thiocyanide (CNS) and sodium (Na). The data also show that other attenuation mechanisms were operative, the nature of which is not known but assumed to have been related to soil-contaminant interactions.

For the contaminants iron (Fe), vanadium (V) and to some degree total organic carbon (TOC), "dilution" played a minor role compared to the other mechanisms involved. It was assumed that the formation and filtration of the iron (Fe) and vanadium (V) precipitates would be the major removal mechanism.

The removal mechanisms for total organic carbon (TOC) in part would be via some biological degradation but because of the short duration of the tests biological decomposition was not felt to be fully developed. Therefore the primary attenuation mechanism was thought to be sorption of the organics onto the soil.

TABLE 5. CUMULATIVE NET ATTENUATION OF STRETFORD LIQUOR CONTAMINANTS IN SOIL 1

Contaminant	Batch Reactor Series	Attenuation with"Dilution" mg/gm	Attenuation minus"Dilution" mg/gm
S_2O_3	R	5.27	2.00
	D1	-1.151	- .013
	D2	- .684	0.0
	D3	- .176	- .04
	D4	- .223	- .016
	D5	-	-
CNS	R	16.962	1.212
	D1	-6.092	0
	D2	-1.108	0
	D3	- .369	- .004
	D4	- .435	- .001
	D5	- .301	0
Pb	R,D1,D2	0	0
Cd	R,D1,D2	0	0
Fe	R	.01	.002
	D1	- .001	0
	D2	0	0
V	R	.016	.014
	D1	- .001	0
	D2	- .001	0
	D3	0	0
	D4	0	0
	D5	0	0
TOC	R	4.016	1.58
	D1	- .398	.001
	D2	- .225	- .001
	D3	- .025	+ .001
	D4	- .01	- .005
	D5	- .058	- .007
Na	R	10.885	1.786
	D1	-2.5	- .008
	D2	-1.435	- .036
	D3	- .79	0
	D4	- .299	- .009
	D5	- .134	.002

Tables 5, 6 and 7 show that as the clay content of the soil increases the amount of thiosulphate (S_2O_3), thiocyanide (CNS), iron (Fe) and vanadium (V) attenuated by mechanisms other than "dilution" also increases. For example, the cumulative net attenuation including "dilution" of thiocyanide (CNS) is 16.962, 18.431 and 19.456 mg/gm respectively for Soils 1, 2 and 3. However the cumulative net attenuation minus "dilution" is 1.212, 4.872 and 4.789 mg/gm for thiocyanide (CNS) in Soils 1, 2 and 3.

This trend of increased cumulative net contaminant attenuation including "dilution" with increased clay content is compatible with expectations since clay, of all the soil types, is considered to be most active in soil-contaminant interactions.

The data presented for lead (Pb) and cadmium (Cd) warrant some explanation. They exhibit no calculated attenuation. This is not however the case. Since the

TABLE 6. CUMULATIVE NET ATTENUATION OF STRETFORD LIQUOR CONTAMINANTS IN SOIL 2

Contaminant	Batch Reactor Series	Attenuation with "Dilution" mg/gm	Attenuation minus "Dilution" mg/gm
S_2O_3	R	5.367	2.617
	D1	-1.798	- .01
	D2	-1.032	- .002
	D3	- .554	- .001
	D4	- .294	- .009
	D5	- .123	0
CNS	R	18.431	4.872
	D1	-2.958	0
	D2	-1.783	0
	D3	-2.218	- .001
	D4	- .788	0
	D5	- .397	0
Pb	R,D1,D2	0	0
Cd	R,D1,D2	0	0
Fe	R	.011	.005
	D1	- .001	0
	D2	0	0
V	R	.017	.016
	D1	- .001	0
	D2	- .001	0
	D3	0	0
	D4	0	0
	D5	0	0
TOC	R	4.847	3.683
	D1	- .422	0
	D2	- .302	- .005
	D3	- .033	.001
	D4	- .016	- .002
	D5	- .06	- .01
Na	R	12.309	5.449
	D1	-2.453	- .005
	D2	-1.865	- .022
	D3	- .865	.003
	D4	- .399	- .017
	D5	- .217	- .004

TABLE 7. CUMULATIVE NET ATTENUATION OF STRETFORD LIQUOR CONTAMINANTS IN SOIL 3

Contaminant	Batch Reactor Series	Attenuation with "Dilution" mg/gm	Attenuation minus "Dilution" mg/gm
S_2O_3	R	6.619	5.423
	D1	- .658	- .009
CNS	R	19.456	4.789
	D1	-3.158	0
Pb	R,D1	0	0
Cd	R,D1	0	0
Fe	R	.014	.009
	D1	0	0
V	R	.018	.018
	D1	0	0
TOC	R	4.348	2.19
	D1	- .452	.001
Na	R	12.697	4.819
	D1	-2.289	- .004

concentrations in the waste are small, 3.2 mg/l and 0.46 mg/l respectively, the masses attenuated in mg/gm soil are extremely small numbers and appear as "0" in the tables.

The experimental data showed that the concentrations of calcium (Ca), magnesium (Mg) and aluminum (Al) increase during passage of the industrial wastes through the soil. This was postulated to be due to the solubilization of soil constituents and the release of ions into solution during ion exchange reactions. This trend is not unlike that exhibited in the field.

It is to be noted that the soil water does act to "dilute" the soil constituents dissolved by the above process. This effect of "dilution" was observed to occur for dissolved aluminum where the attenuation minus "dilution" exceeded that of the total attenuation. Only at the time that the corrosive nature of the soil would be decreased would "dilution" overcome the effect of solubilization.

Contaminant Desorption

Tables 5, 6 and 7 presents the contaminant desorption character of the industrial waste. The desorption experiments are referred to as D1 through D5 with desorption indicated by a negative sign (negative attenuation).

It is seen that some measure of desorption was experienced for most contaminants. As might be expected, desorption was extensive for these contaminants for which "dilution" through interchange between the waste and the soil water was a major mechanism of concentration reduction. The continous passage of desorption water eventually removes all of the contaminants in the soil. Contaminants exhibiting extensive "dilution" as described above included thiosulphate (S_2O_3), thiocyanide (CNS) and sodium (Na) for the Stretford liquor.

Active desorption was not exhibited on the contaminants for which the attenuation mechanisms other than "dilution" were prominent. This is most clearly depicted for vanadium (V) in the Stretford liquor. In the three soils, the average mass of vanadium (V) attenuated across the five reactors was 0.017 mg/gm soil with an average of 0.016 mg/gm soil due to processes other than "dilution". Correspondingly, almost none of the contaminant was removed during desorption. This suggests the presence of a long-term attenuation mechanism. Similar characteristics were exhibited for iron(Fe).

The desorption process causes migration of the contaminants in the down flow direction. However, even for the actively desorbing contaminants, the peak concentration per desorbing slug reduces with increased desorption.

Projection to Field Condition

Previously the calculation methodology to plot C/C_0 versus gm soil/ml of waste was discussed. The curves generated for sodium (Na) and vanadium (V) in the Stretford Liquor passing through Soil 2 are used for discussion and are presented in Figures 5 and 6 respectively.

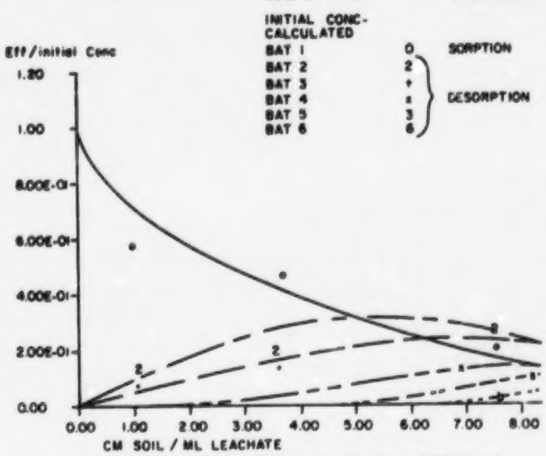

FIGURE 5. STRETFORD LIQUOR SORPTION & DESORPTION OF SODIUM IN SOIL 2

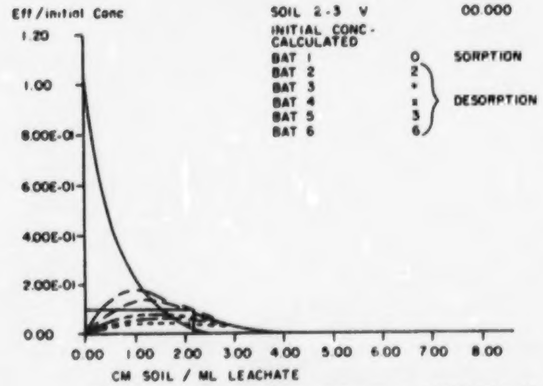

FIGURE 6 STRETFORD LIQUOR SORPTION & DESORPTION OF VANADIUM IN SOIL 2

As identified previously, the primary mode of sodium (Na) concentration reduction in the soil was "dilution". Consequently, active desorption was also the case. These observations are clearly shown in Figure 5. The concentration of the sodium (Na) reduced as the slug of Stretford liquor moved through the soil (as gm soil/ml leachate increases). Figure 5 also shows the concentration of sodium (Na) as the 5 desorption slugs (Batch 2 through Batch 6) moved sequentially through the soil. Note that the concentration of sodium (Na) in the soil reduces with increased desorption. For the third and successive desorption slugs the peak concentration of the sodium were not found in the five reactors used.

In the case where the peak concentration of the desorption slugs could be plotted the curve could be used to determine the ratio of gm of soil/ml of leachate, required to achieve some desirable concentration. Figure 6 is suitable for this purpose.

The initial concentration of vanadium (V) in the Stretford liquor was 90 mg/l. Assuming a tolerable concentration of 9 mg/l a value of $C/C_0=0.1$ is calculated. Figure 6 shows that a line has been projected horizontally from the ordinate at $C/C_0=0.1$ to intersect the curve of peak desorption concentrations at approximately 2.2 gm soil/ml of leachate. The interpretation of this analysis is as follows.

Reference is made to the initial passage of industrial waste through the soil. A ratio of 2.2 gm soil/ml of waste fixes a point in space depending on the amount of waste applied to the soil. The assumption is that the soil to waste ratio is independent of the geometry of the application of the waste to the soil.

However, under a given geometry of application, the ratio of 2.2 gm soil/ml of waste fixes a point in space some distance downflow. The distance is determined from the application geometry and the density of the soil. The data in Figure 6 shows that the ratio of $C/C_0=0.1$ occurs between the 2nd and 3rd desorption slugs at approximately 2.5 slugs. Thus the concentration of 9 mg/l is reached at the predetermined point downflow after 2.5 ml of desorption water per ml of waste has passed through the soil.

From an assumed 15 foot application of

Stretford Liquor to a soil represented by Soil 2 with an in-plate density of 95 lbs/ft^3 on a dry weight basis, the vanadium concentration downflow from the base to the landfill can be calculated. From the graphs of Stretford liquor migration through Soil 2 it is calculated that at a distance of 22 feet from the base of the landfill the concentration of vanadium (V) would be 9 mg/l. Vanadium concentrations at this point have been reduced to tolerable concentrations. However, the concentration of other contaminants have not been reduced to tolerable concentration levels.

Table 8 presents the calculated concentrations of various contaminants at the distance of 22 feet from the base of the landfill for the above considered disposal of Stretford liquor. Table 6 indicates that while the concentration of vanadium (V) at a distance of 22 feet from the base of the landfill has reached a tolerable concentration, the water is highly polluted.

TABLE 8. CALCULATED GROUNDWATER CONTAMINANT CONCENTRATION

Stretford Liquor Contaminant	Peak Contaminant Concentrations at Noted Distance From Base of Fill mg/l 22 feet
Vanadium	9 mg/l
TOC	12960
S_2O_3	22785
CNS	92730
Na	47300
Pb	3.14
Cd	.3
Fe	48.72

The above calculations do not take into account lateral dispersion of the migrating contaminants nor microbial decay. This serves as a factor of safety for the analyses.

It would be recommended that for purposes of design a factor of safety, maybe 2.0, be applied to the calculations.

CONCLUSIONS

1. "Dilution" is an important mechanism of attentuation for all of the liquid waste contaminants. By "dilution" alone or diffusion and dispersion it is possible to reach a tolerable contaminant concentration in a hydrogeologic environment downflow from the point of disposal in land.

The contaminants attenuated primarily by "dilution" for the Stretford liquor were thiosulphate (S_2O_3), thiocyanide (CNS) and sodium (Na).

The contaminants which were primarily attentuated by mechanisms other than "dilution" were lead (Pb), cadmium (Cd), iron(Fe) and vanadium (V).

The contaminants attenuated by a combination of "dilution" and other mechanisms was total organic carbon (TOC).

Contaminants which desorbed during waste migration through the soil were:
Stretford liquor: calcium (Ca), magnesium (Mg), aluminum (Al)
Alkaline cleansing: calcium (Ca), magnesium (Mg), aluminum (Al).

2. Desorption was exhibited by all contaminants studied and was most prominent for those which were attenuated primarily by the mechanism of "dilution". These include thiosulphate (S_2O_3), thiocyanide (CNS) and sodium (Na). However the peak migrating desorption concentration reduces as the amount of desorption increases. Eventually a tolerable concentration in the soil water is reached.

For those contaminants attenuated primarily by mechanisms other than "dilution" such as iron (Fe) and vanadium (V) desorption at any time was limited.

It could be anticipated that desorption processes would be complete over geologic time spans.

3. Attenuation data collected from the dispersed soil experimentation can be used to project soil water concentrations in a field situation by the use of a correction factor f_E. While this factor was not determined for this project, data from parallel experimentation was considered to be suitable.

For design purposes it is suggested that a factor of safety of 2 be applied to the experimentally calculated soil water concentrations downflow from the base of the disposal site.

The attenuation data also can be used for input to the SWIMP for the evaluation of potential disposal sites.

4. The Stretford liquor from a steel plant could be disposed of on land in an

environmentally controlled manner. The waste loading, opportunity for "dilution" and subsequent desorption would determine the time and space parameters defining the zone of influence of the disposal operation.

5. The zone of influence of the disposal operation is closely related to the waste loading. In this regard the data suggests that a number of small waste disposal sites with a limited zone of influence are preferable to a large site with a large zone of influence. It can be postulated that the past practice of waste disposal in small sites may account for the limited environmental impact measured to-date.

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ESTIMATION OF NONREACTIVE AND REACTIVE SOLUTE FRONT LOCATIONS IN SOILS

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ABSTRACT

A technique, based on the physical principles of water and solute transport, was used to describe the position of nonreactive and/or reactive solute fronts in a soil profile. The procedure estimates the solute front location after infiltration and redistribution of the soil water to "field capacity", and includes extraction of soil water by plant roots between irrigation/rainfall events. Linear equilibrium adsorption-desorption of the reactive solutes was assumed. The approximation procedure was based on the principles that (i) the soil water residing in all pore sequences participates in the transport processes, and (ii) the soil water initially present in the profile is completely displaced ahead of the water entering at the soil surface. An analysis of published field and laboratory data on infiltration of nonreactive solutes (Cl^- and NO_3^-) indicated that these assumptions were valid. Agreement between predicted solute front location using a sophisticated one-dimensional transient flow models and the above procedure further support the validity of the assumptions. Field data for chloride movement in a sandy soil, in the presence of a fully established millet crop, during a 60-day period were in agreement with the simplified model. The major drawback of the present technique is in its failure to describe the attenuation or spreading of a solute pulse as it is leached through the soil profile.

The movement of chemicals through the soil is influenced by several physical and chemical properties of the soil and solute. Complex interactions between the solute and soil matrix (hydrodynamic dispersion, adsorption-desorption, chemical/biological transformations, etc.) play an important role in solute mobility and concentration distribution in the soil profile. Mathematical models and numerical solutions of these conceptual process-oriented models are available (3, 9, 12, 15, 16). However, because of the complexity and number of input parameters required to solve these models, they have not been used, in general, to simulate field cases.

A technique, based on the physical principles of water and solute transport, was used to describe the position of nonreactive and/or reactive solute fronts in a soil profile. The procedure estimates the solute front location after infiltration and redistribution of the soil water to "field capacity", and includes extraction of soil water by plant roots between irrigation/rainfall events. Published data on solute transport, for laboratory and field conditions, were used to validate the model.

COMPUTATIONAL METHODS

The computational techniques presented here are limited to estimating the position of an invading solute front. The spreading of the solute zone behind the front due to molecular diffusion and convective dispersion is not considered here. The technique is based on the principal assumptions that (i) the soil water residing in all pore sequences participates in the transport processes, and (ii) that the soil water initially present in the soil profile is completely displaced ahead of the water entering at the soil surface. A simple model for prediction of water and sediment transport from a watershed was developed

(5) based on these assumptions.

Infiltration

Consider the infiltration of an amount of water, I, into a homogeneous soil profile with a uniform initial soil-water content fraction of θ_i (cm^3/cm^3). The depth to which the wetting front will advance can be calculated from

$$d_{wf} = \frac{I}{\theta_f - \theta_i} \quad , \quad \theta_f > \theta_i \qquad [1]$$

where, d_{wf} is the distance (cm) from the soil surface to the wetting front, and θ_f is soil water content in the wetted zone behind the wetting front. For infiltration of 5 and 10 cm of water into an initially dry (θ_i=0) soil, the wetting front depth (d_{wf}) would be 14.3 and 28.6 cm, respectively, when θ_f=0.35 cm^3/cm^3 (Figure 1). However, if θ_i was 0.10 cm^3/cm^3 and θ_f was 0.35 cm^3/cm^3, the wetting front would be at 20 and 40 cm, respectively, for 5 and 10 cm water applications (Figure 2). Therefore, for a given water application and θ_f, the wetting front depth increases as θ_i increases.

If assumptions (i) and (ii) given above are valid, then the water at the observed wetting front for $\theta_i > 0$ is the water initially contained in the soil profile and not that added at the soil surface. Hence, complete displacement of the initial water ($\theta_i > 0$) results in a nonreactive solute front being located at,

$$d_{sf} = \frac{I}{\theta_f} \qquad [2]$$

where, d_{sf} is the solute front position (cm). Solving equation [1] for I and substituting in equation [2] yields,

$$d_{sf} = d_{wf}\left[1 - \frac{\theta}{\theta_f}\right] \quad , \quad \theta_f > \theta_i \qquad [3]$$

or, upon rearrangement,

$$\frac{d_{sf}}{d_{wf}} = 1 - \frac{\theta_i}{\theta_f} \quad , \quad \theta_f > \theta_i \qquad [4]$$

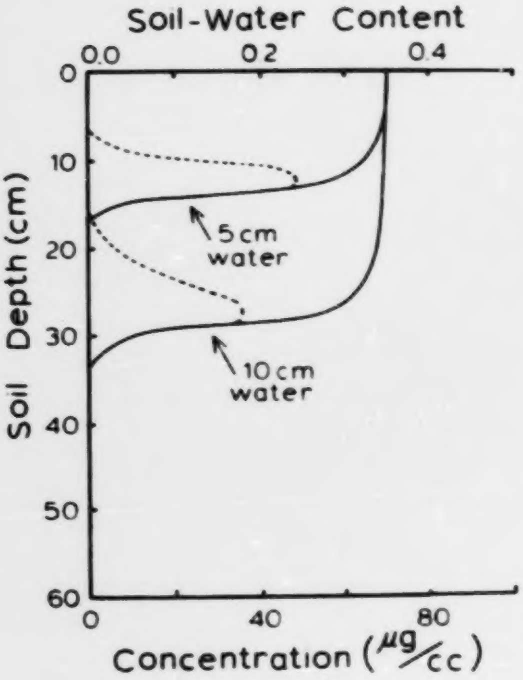

Figure 1. Distribution of water (solid line) and nonreactive solute (dashed line) after 5 and 10 cm of water had infiltrated into an initially dry (θ_i=0) soil profile.

Given the values of θ_i and θ_f, the apparent retardation of the nonreactive solute front with respect to the observed wetting front can be estimated by equation [4]. Note that the value of the ratio (d_{sf}/d_{wf}) is equal to 1.0 when θ_i=0 (i.e., infiltration into dry soil); thus the nonreactive solute front rides on the wetting front. However, when $\theta_i > 0$ (i.e., infiltration into moist soil), the nonreactive solute front would lag behind the observed wetting front [(d_{sf}/d_{wf}) < 1]. Equation [4] is not valid for the case of θ_i=θ_f, as the ratio (d_{sf}/d_{wf}) is equal to zero.

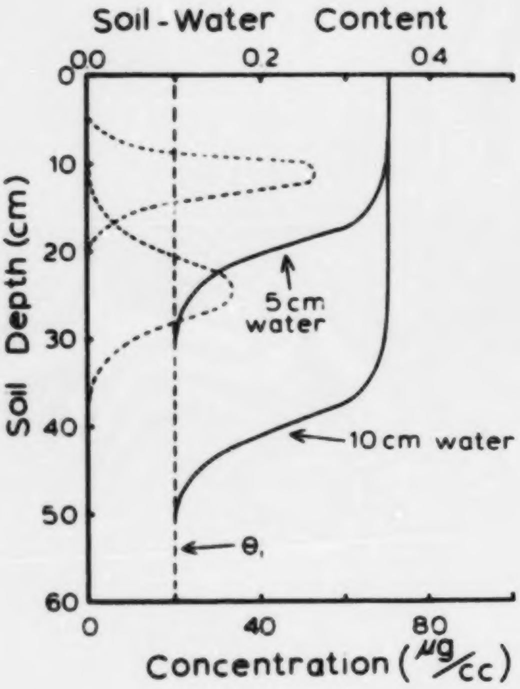

Figure 2. Distribution of water (solid line) and nonreactive solute (dashed line) after 5 and 10 cm of water had infiltrated into a soil profile at a uniform initial water content (shown as vertical dashed line) of 0.1 cm^3/cm^3.

Note that the nonreactive solute front position depends on the amount of water added and the average water content in the wetted zone behind the wetting front, but not on the initial water content (Figures 1 and 2). This conclusion is in agreement with experimental observations of previous workers (1, 9, 10, 16).

Published data for NO_3^- and Cl^- movement in several soils were used to test the validity of assumptions (i) and (ii). These data are presented in Figure 3 using equation [4]. Considering the wide range in experimental conditions and that both laboratory and field data were included, the agreement between the 1:1 line and the data is excellent. Apparently, in all the cases considered, the initial soil water in the profile was displaced ahead of the applied water; thus, supporting our principal assumptions.

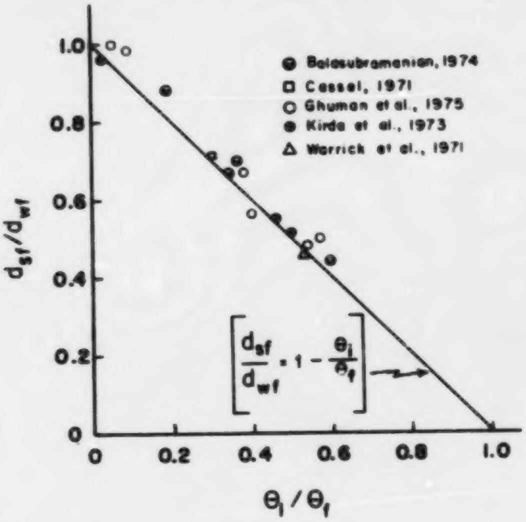

Figure 3. Comparison of experimentally measured values (data points) and calculated values (solid line) of the ratio d_{sf}/d_{wf} as a function of θ_i/θ_f.

It has been suggested that the soil water within the intra-aggregate micropores may be excluded from solute transport processes; thus, assumption (ii) may not be valid for well-aggregated soils. Assuming an analogy between heat and solute transfer in spheres, the *characteristic time* (t_o) required for 99% of the solute to diffuse out of an aggregate can be calculated by (13),

$$t_o = (0.1012)\left(\frac{d^2}{D_o \tau}\right) \qquad [5]$$

where, d is aggregate diameter (cm), D_o is molecular diffusion coefficient (cm^2/min) in water, and τ is tortuosity factor to account for intra-aggregate geometry. The dependence of t_o on d, as developed in equation [5], is graphically presented in Figure 4 for several values of τ. It is apparent that the characteristic times (t_o) are small (< 15 minutes) and that the influence of τ is not significant for small aggregates ($d < 0{\cdot}2$ cm). Other workers (4, 12) have also reached similar conclusions regarding the significance of aggregate diameter for absorption of water and diffusion of gases in aggregated media.

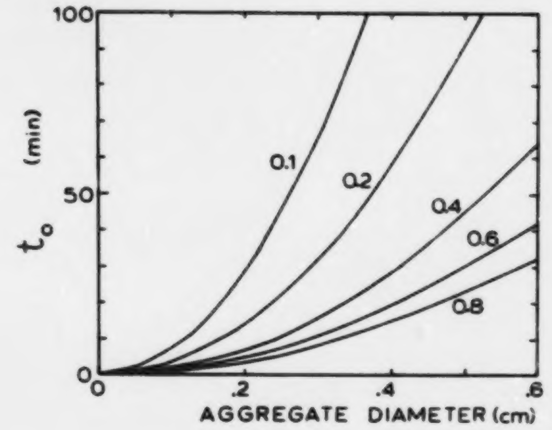

Figure 4. The relationship between aggregate diameter (d) and the characteristic time (t_o) for 99% mass transfer. Numbers shown along each curve are the values of intra-aggregate tortuosity (τ).

A *characteristic critical velocity* (V_c), above which intra-aggregate diffusion becomes significant, may be calculated from:

$$V_c = \frac{d}{t_o} \quad [6]$$

The dependence of V_c on d and τ is shown in Figure 5. For aggregates with $d < 0.2$ cm (most common size used in laboratory column studies), it would appear that intra-aggregate diffusion becomes significant only when $V_c > 4$ cm/hr. Such velocities are not generally encountered in most field or laboratory studies. Thus, it may be concluded that for most aggregated soils, all the soil water participates in the solute transport process.

Redistribution of Soil-Water

At the termination of infiltration, the soil water content in the wetted zone decreases due to drainage or redistribution until the profile attains a "field capacity" water content (θ_{FC}). The movement of the solute front due to this process is determined by the amount of "drainable" water above the depth d_{sf}. It can be shown that,

$$d'_{sf} = d_{sf} + \frac{(d_{sf})\ (\Delta\theta)}{\theta_{FC}} \quad [7]$$

where, d'_{sf} is solute front location after redistribution, $\Delta\theta = (\theta_f - \theta_{FC})$, and the product $(d_{sf})\ (\Delta\theta)$ represents the amount of "drainable" water above d_{sf}.

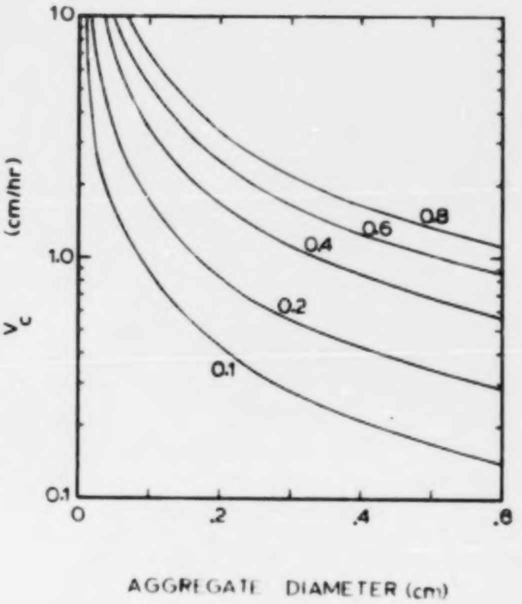

Figure 5. The relationship between aggregate diameter (d) and the characteristic critical velocity (V_c). The numbers shown along each curve are the values of intra-aggregate tortuosity factor (τ).

Substitution of equation [3] for d_{sf} in equation [7] yields,

$$d'_{sf} = \frac{I}{\theta_{FC}} \quad [8]$$

The validity of equation [8] is limited to the case where the solute front is initially located at the soil surface (z=0) prior to infiltration. For a case when the solute front is located at some depth d_i ($d_i > 0$) before infiltration, equation [8] must be modified as,

$$d'_{sf} = d_i + \frac{I}{\theta_{FC}} \quad [9]$$

The mobility or depth to which a reactive solute front penetrates is reduced due to adsorption-desorption processes. By assuming a linear and reversible equilibrium adsorption model, a retardation factor (R) can be calculated (3),

$$R = 1 + \frac{\rho k}{\theta_{FC}} \quad [10]$$

where, ρ is soil bulk density (g/cm^3), k is adsorption partition coefficient (cm^3/g), and θ_{FC} is field capacity water content (cm^3/cm^3).

Equation [9] can be generalized to predict reactive front locations,

$$d'_{sf} = d_i + \frac{1}{R}\frac{I}{\theta_{FC}} \quad [11]$$

where, R is defined by equation [10]. For a nonreactive solute (k=0) the retardation factor R=1, and equation [11] reduces to equation [9]. Note that d'_{sf} of a previous event becomes d_i for the next event.

Plant Root Extraction of Soil Water

Many practical solute transport problems occur in the presence of a growing crop. Extraction of water from the rooting zone results in a nonuniform water content profile. Because of this several modifications must be made in the equations presented in the preceding sections. The extraction of soil water by the plant was simulated by a macroscopic model (11),

$$\frac{\partial\theta(z,t)}{\partial t} = T \cdot \frac{K(\theta) \cdot A(Z)}{\int_0^L K(\theta) \cdot A(Z)\, dz} \quad [12]$$

where, $\partial\theta/\partial t$ represents the change in water content due to roots $K(\theta)$ is soil hydraulic conductivity (cm/hr), A(Z) is effective plant root absorption function which was assumed to be proportional to root density distribution, T is evapotranspiration demand (cm/hr), and L is the rooting depth. Equation [12] distributes the evapotranspiration demand (T) over the entire rooting zone according to the product $[A(Z)\cdot K(\theta)]$. A "static" soil profile is assumed where the vertical flow of water is ignored.

Depletion of water by plant roots creates a soil-water *deficit* in the profile. The deficit above the solute front, denoted I_d, is

$$I_d = \int_0^{d_{sf}} [\theta_{FC} - \theta(z)]\, dz \quad [13]$$

where, the water content profile $\theta(z)$ is predicted by equation [12] at any time, and d'_{sf} is defined by equation [11]. The deficit (I_d) must be satisfied by an input (I) due to a irrigation/rainfall event before further movement of the solute front can occur. Furthermore, the evapotranspiration losses during the redistribution period, assumed here to be two days, must also be accounted for in calculating the "effective" amount of input water (I_e) resulting from a rainfall/irrigation event. This is done as follows:

$$I_e = I - [I_d + (2)\ (T)] \quad [14]$$

For the case when the deficit is overcome by an event (i.e., $I_e > 0$), the new location of the solute front may be calculated as,

$$d_{sf} = d_i + \frac{I_e}{\theta_{FC}} \cdot \frac{1}{R},\ I_e > 0 \quad [15]$$

However, for the case when an event is not large enough to overcome the deficit (i.e., $I_e \leq 0$), there is no additional movement of the solute front,

$$d_{sf} = d_i \ ,\ \ I_e \leq 0 \quad [16]$$

The input water, after adjusting for the two-day evapotranspiration loss, was distributed in the soil profile to a depth d_x by successive interations to satisfy the condition,

$$(I - 2T) = \int_0^{d_x} [\theta_{FC} - \theta(z)] dz \ ; \quad d_x \leq d_{sf} \quad [17]$$

All calculations involving root extraction were performed on an IBM 360/370 digital computer (FORTRAN IV program). Average computer costs for a 60-day simulation period were less than five dollars.

MODEL VALIDATION

Leaching of a chloride pulse through a Eustis fine sand field profile, with a fully established crop of millet *(Panicum milaceum)*, was measured (7) during a 60-day period between August 1-September 24, 1973 at Gainesville, Florida. The chloride data was used to validate the present model. Experimentally measured (8) soil hydraulic conductivity versus soil-water content for the same field plot was fitted to the following relationship:

$$K(\theta) = \text{Exp}\ [B\theta^{\alpha} + D] \qquad [18]$$

with $B = -3.3471$, $\alpha = -0.62$, and $D = 10.1753$. The effective root absorption function, $A(z)$, was assumed to be,

$$A(z) = \text{Exp}\ [-0.005z] - 0.471 \qquad [19]$$

where, z is soil profile depth. Equation [19] describes an exponential decay root absorption function, where 39, 28, 19, 11, and 3% of the total root activity was present in each successive 30 cm segments of the soil profile to 150 cm. The evapotranspiration demand (T) was assumed to remain constant at 0.3 cm/day during the 60-day simulation period. The rainfall distribution at the experimental site was also recorded (7), and used as input in the present model. The Eustis soil profile drains to a field capacity (θ_{FC}) of 0.08 cm^3/cm^3 two-days after any input event. Plant available water was defined to be that held in the profile between field capacity (θ_{FC}) and 15-bar value ($\theta_{15}=0.03$) water contents.

Experimentally measured (7) field data for chloride front location and that estimated by the present model are compared in Figure 6. Considering all the simplifying assumptions in the model, the agreement between measured and predicted values is very good; thus, validating the model.

An exact knowledge of the root absorption function [A(z)] for a given crop is often unavailable. In such cases, a uniform extraction of soil water throughout the rooting depth, i.e., A(z)= constant, may be assumed without introducing serious error in the prediction of solute front locations. The magnitude of such error was between 5-15% for the case of Cl^- movement in Eustis sand (data of Figure 6).

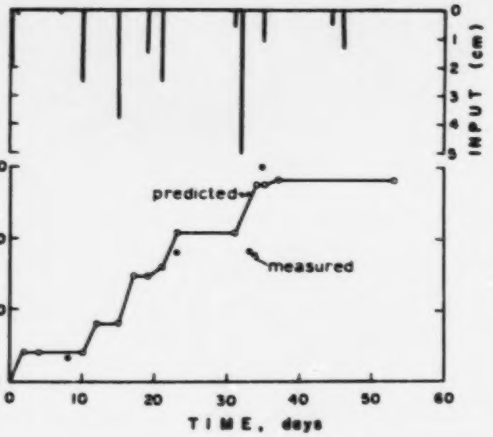

Figure 6. Comparison of the Cl^- front locations predicted (solid lines connecting open circles) and those experimentally measured (closed circles) on a Eustis fine sand profile with a fully grown crop of millet.

The influence of adsorption-desorption processes in retarding the movement of a reactive solute is demonstrated in Figure 7. The rainfall distribution data, K(θ), and A(z) functions were identical to those used in Figure 6. A value of R=1 represents the case of no adsorption (nonreactive solutes), while R=2 and 4 represent the case of reactive solutes. From the curves shown in Figure 7, it is apparent that the efficiency of any given rainfall event in moving the solute front decreased as R increased (see Eq. 11). Since the reactive solute front remains closer to the soil surface than a nonreactive solute front, a larger fraction of the water input may be effective in leaching the reactive solute. However, a given amount of water input is four-times less efficient (for R=4) in moving the reactive solute front than a nonreactive solute front (R=1). This results in the reactive solute front movement being retarded as shown in Figure 7.

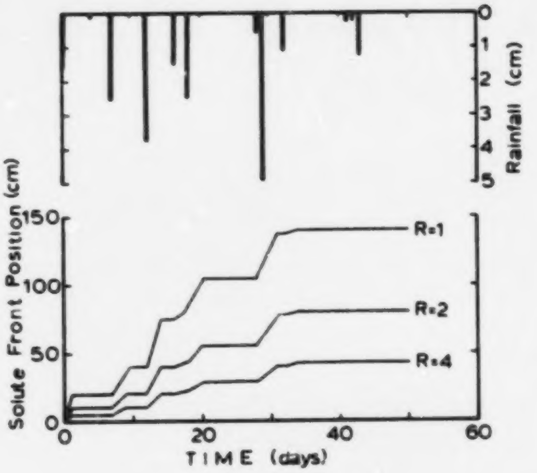

Figure 7. Influence of adsorption-desorption processes in retarding the reactive solute front movement in a soil profile. R=1 represents the nonreactive solutes.

DISCUSSION

The model presented here is intended to be a management model, which estimates the solute front position. The procedure does not predict the solute concentration distribution in the soil profile. The model is limited to the case of homogeneous, well-drained soil profiles. Cases where the soil profile is layered or the water table is close to the soil surface were not considered in the present model. However, based on transport studies for reactive solutes through multi-layered soils (15), the proposed model could be adapted to predict the time of arrival of the solute front at a given depth (such as at the water table) by obtaining a weighted-mean of the retardation factors for each soil layer.

The adsorption of the reactive solutes was assumed to be described by a linear adsorption isotherm. When the adsorption isotherm is nonlinear, the retardation factor (R) is not a constant as shown in eq. [10], but is concentration-dependent. However, a weighted-mean R value may be used (14) to predict the movement of reactive solute fronts.

Two additional processes not accounted for in the present model are (i) plant uptake of the solutes, and (ii) chemical and/or microbiological transformations of the solutes. Efforts are currently underway in our laboratory to improve the present model capabilities by incorporating both these processes.

ACKNOWLEDGMENTS

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TRACE ELEMENT MIGRATION IN SOILS:
DESORPTION OF ATTENUATED IONS AND EFFECTS OF SOLUTION FLUX

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ABSTRACT

A leachate from a simulated sanitary landfill was individually spiked with ten trace elements (As, Cd, Cr, Cu, Hg, Ni, Pb, Se, V, Zn) and used to leach eleven soils from the seven most prominent orders. When the leaching was concluded, each soil column was segmented into ten sections which were extracted with water and with 0.1 N HCl. Results indicate that the ions sorbed initially were retained most tightly, and that coarse textured soils most easily release sorbed ions. Extraction with water releases only a minimal quantity of attenuated ions. Dilute acid leaching, in contrast, dissolves significant quantities of sorbed ions even though it is preceded by complete drying of the soil. Additionally, the leaching work displayed a dependence of the mobility of certain ions to changes in flow rate. Accordingly, preliminary data are presented which demonstrate the potential of controlling solution flux in order to optimize trace element attenuation.

INTRODUCTION

Land disposal of municipal and industrial wastes is increasing rapidly (U.S. EPA 1973). These wastes may contain potentially hazardous concentrations of toxic materials (Ross 1968, Nemerov 1971). Much current effort, therefore, has focused on the ultimate fate of trace contaminants in the environment (Page 1974, Lisk 1972).

In a previous report (Korte et al. 1976) equations were developed to predict the movement of eight trace elements (As, Be, Cd, Cr, Ni, Se, V, Zn) through soils with varying properties. Where the dependent variables were clay content, surface area, and the content of free iron oxides, predictive equations were significant at the 99% confidence interval for the migration of Cd, Be, Zn, and Ni, and at the 95% interval for As and V. By including pH as a dependent variable the prediction of Cr and Se was significant at the 95% level. Cu and Pb did not migrate through the soil columns so their behavior in the time frame of that experiment was unrelated to soil properties.

Despite statistical correlations, actual mechanisms usually have not been identified. This fact, coupled with demonstrations that soils can release potential pollutants when leached with various solutions (Fuller et al. 1976), indicates that the permanence of land disposal is unknown. Rouston and Wildung (1969) suggested the non-permanence of land disposal, but quantitative data are lacking.

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Extraction Studies

One way to evaluate the permanence of ion attenuation is by relating it to the efficiency of extraction techniques. The availability of trace metals for plant growth has long been determined by extraction (Black 1965, Walsh and Beaton 1973, Krauskopf 1972). Since mild extractants reflect plant availability better than total analyses (Ivanov 1969), it follows that conditions of natural leaching are best simulated by a mild extractant. Indeed, to determine what portion of attenuated metal ions are subject to leaching by rain water, extraction with water would be useful.

Extractions with harsher reagents also can provide important information. Simple "input-output" data do not completely describe an element's migration. A major shortcoming is encountered if none of the element passes through the soil column during the experiment. It is then impossible to determine if the soil's characteristics are affecting the ion's movement. In any case, knowledge of the distribution of a sorbed element in a profile or soil column yields greater insight into the soil's capacity for retention of the element.

Quantitative interpretation of extraction data, however, must be made cautiously. Hodgson (1960) showed that heavy metal sorption is not completely reversible. In his experiment, non-extractable, sorbed Co was considered to be a result of interlattice penetration. It is clear that whatever mechanisms are involved, depending upon the capacity and thermodynamic favorability of competing sorbing reactions, an extractant would remove different percentages of sorbed material from varying depths in a soil column or profile.

Therefore, the objective of this work was to determine the distribution of ten sorbed elements (As, Cd, Cr, Cu, Hg, Pb, Ni, Se, V, Zn) in soil columns by means of both a water and dilute acid extraction. These data provide quantitative information on the potential for desorption of the attenuated ions, as well as further verification of the role of soil properties in trace element attenuation.

Studies of Solution Flux

It has been previously emphasized that little is known about actual mechanisms (Fuller and Korte 1975) of trace element attenuation. Soil texture has been repeatedly singled out as an important factor in trace element migration. However, whether this is due primarily to surface effects or the consequent effects on flow has not been characterized. Previous work, especially by Biggar and Nielsen in 1960, has indicated that the migration of ions is strongly influenced by the flow rate of the leaching solution. Leaching studies in this laboratory using a conventional constant head arrangement resulted in pseudo-steady-state flow conditions. Small changes in flow due primarily to trapped gas caused an erratic output. Accordingly, experiments were begun to examine the effects of solution flux or flow rate on a trace element's migration.

METHODS AND PROCEDURES

Extractions

Ten sorbed trace elements (As, Cd, Cr, Cu, Hg, Ni, Pb, Se, V, Zn) were extracted from soil columns which had been leached with a natural leachate individually spiked with each element. The natural leachate was effluent from a simulated sanitary landfill (Korte, Niebla and Fuller 1976). Trace element concentrations were from 70 to 120 ppm and a leaching rate of 1/2 to 1 pore volume per day was continued for 25 to 30 days. Complete details with respect to apparatus and procedures have been provided elsewhere (Korte et al. 1976).

Eleven soils representing the seven most prominent orders were used in these experiments. Their pertinent characteristics are listed in Table 1. A complete discussion of the soils and their properties has been reported by Fuller et al. (1976).

At the conclusion of the leaching experiments the 5 x 10 cm soil columns were segmented into ten 1-cm sections. Each segment was oven-dried so that a material balance could be easily calculated so that no variations in moisture content would be

Table 1. CHARACTERISTICS OF THE SOILS*

Soil Location	Soil Order	pH	CEC	EC	Surface Area	Free Iron Oxides	Total Mn	Sand	Silt	Clay	Texture Class	Predominant Clay Minerals
			meq/100g	µmhos/cm	m^2	%	ppm	%	%	%		
Wagram (N. Carolina)	Ultisol	4.2	2	225	8.0	0.6	50	88	8	4	loamy sand	Kaolinite Chlorite
Ava (Illinois)	Alfisol	4.5	19	157	61.5	4.0	360	10	60	31	silty clay loam	Vermiculite Kaolinite
Kalkaska (Michigan)	Spodosol	4.7	10	237	8.9	1.8	80	91	4	5	sand	Chlorite Kaolinite
Davidson (N. Carolina)	Ultisol	6.2	9	169	51.3	17.0	4100	19	20	61	clay	Kaolinite
Molokai (Hawaii)	Oxisol	6.2	14	1262	67.3	23.0	7400	23	25	52	clay	Kaolinite Gibbsite
Chalmers (Indiana)	Mollisol	6.6	26	288	125.6	3.1	330	7	58	35	silty clay loam	Montmorillonite Vermiculite
Nicholson (Kentucky)	Alfisol	6.7	37	176	120.5	5.6	950	3	47	49	silty clay	Vermiculite
Fanno (Arizona)	Alfisol	7.0	33	392	122.1	3.7	280	35	19	46	clay	Montmorillonite Mica
Mohave (Arizona)	Aridisol	7.3	10	615	38.3	1.7	825	52	37	11	sandy loam	Mica Kaolinite
Mohave$_{Ca}$ (Arizona)	Aridisol	7.8	12	510	127.5	2.5	770	32	28	40	clay loam	Mica Montmorillonite
Anthony (Arizona)	Entisol	7.8	6	328	19.8	1.8	275	71	14	15	sandy loam	Montmorillonite Mica

* Listed in order of importance

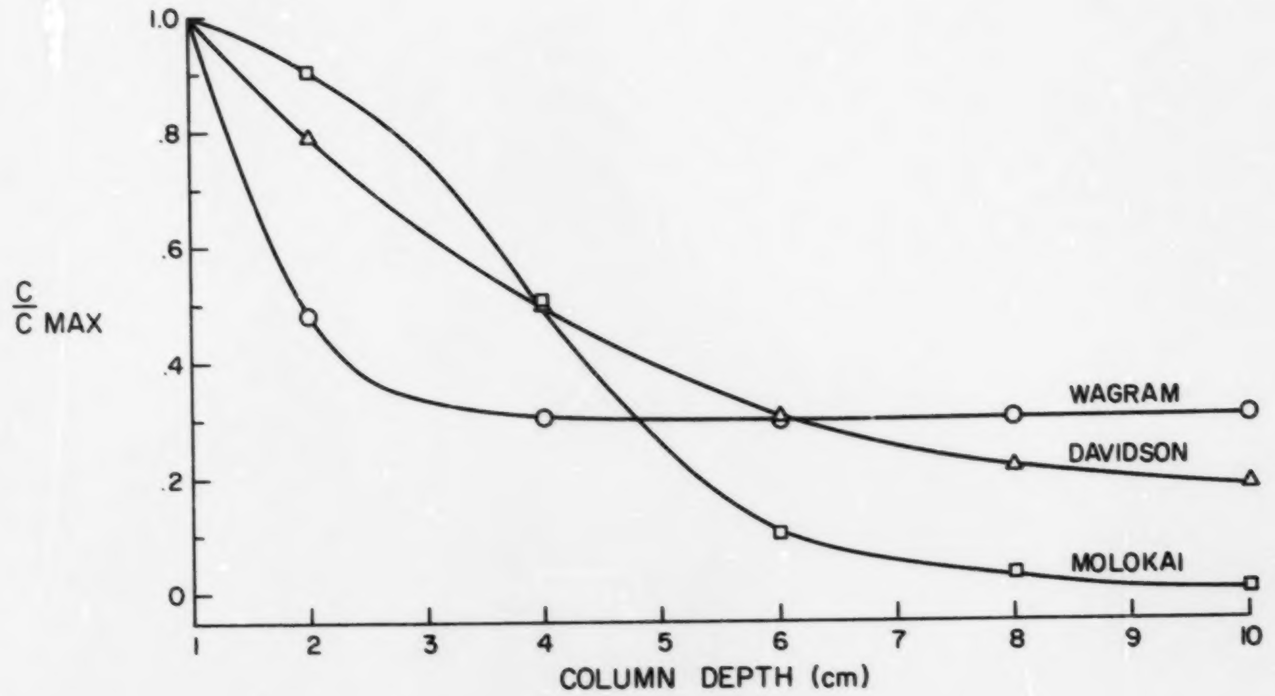

Figure 1. Extraction of Cd from Wagram, Davidson, and Molokai soils.

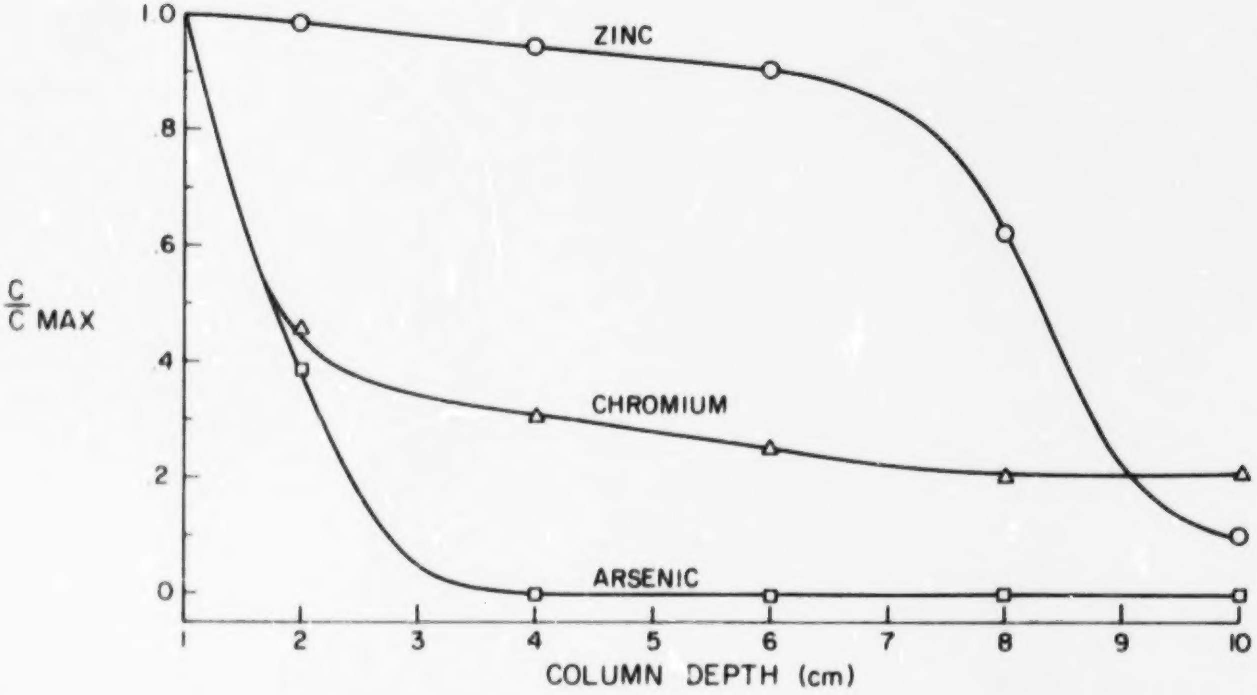

Figure 2. Extraction of Zn, Cr, and As from Davidson clay.

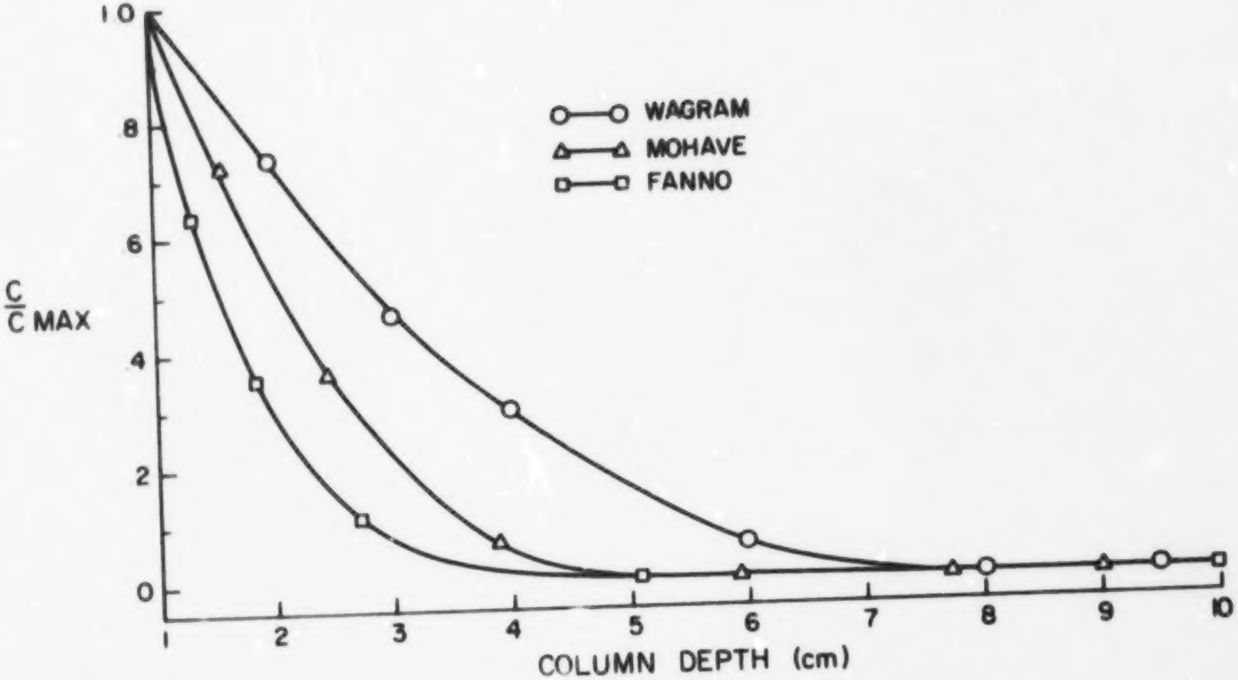

Figure 3. Extraction of Cu from Wagram, Mohave, and Fanno soils.

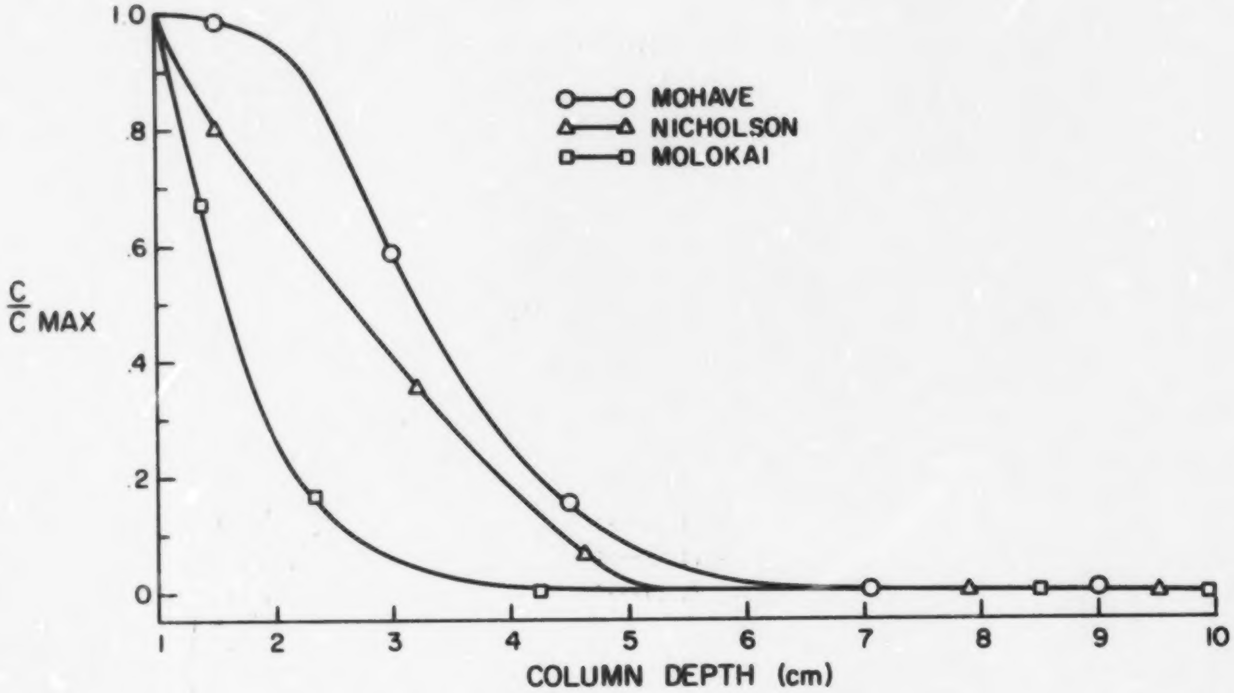

Figure 4. Extraction of Pb from Mohave, Nicholson, and Molokai soils.

involved. Preliminary results showed that variations in extractability for dried versus saturated samples were slight.

Extractions were performed with 0.1 N HCl to obtain a concentration profile of the element for each soil column, and with water to simulate natural leaching. Two grams of dried soil were shaken with 20 ml of extractant for the experimentally determined optimum time. Samples were than centrifuged and filtered. The concentration of the ion in the supernatant was measured by atomic absorption spectrometry and a material balance was calculated.

Solution Flux

For the study of solution flux a uniform flow rate was provided by using Pharmacia (Piscataway, NJ) peristaltic pumps to add leachates to the soil columns. These pumps are capable of flow rates as low as .6 ml/hr with a reproducibility of ±1%. Samples were collected with a fraction collector so that both the flow rate and the trace element concentration could be carefully monitored.

RESULTS AND DISCUSSION

Dilute Acid Extractions

The nature of all soil-trace element relationships when extracting with 0.1 N HCl is represented by the curves in Figures 1 and 2. C_{max} is the maximum concentration in any column segment as determined by the 0.1 N HCl extraction, and C is the concentration determined at other column depths. Almost invariably, C_{max} was the concentration determined from the top segment of the column. By plotting the dimensionless quantity C/C_{max} versus depth, curves for different columns can be easily compared despite variations in concentration among the columns.

Cadmium was not detected in the effluent from the Molokai soil column as evidenced by no Cd being extracted from the last portion of the column (Figure 1). Cadmium breakthrough (effluent conc = influent conc) with Wagram loamy sand is typified by the horizontal portion of the extraction profile. With Davidson clay, the concentration in the effluent leveled off below C/Co (effluent conc/influent conc) = 1.

This range of behavior, as shown in Figure 1, was followed for each soil column and was observed not only for a particular element but also for individual soils (Figure 2). Arsenic was fully retained by Davidson clay, the Zn concentration in the effluent equaled the influent, and Cr attained a steady-state where the influent concentration remained less than the effluent.

Copper and Pb were so immobile in the soils studied that, from input-output data alone, differences due to soil properties could not be distinguished. Some results for the dilute acid extraction for Cu and Pb are shown in Figures 3 and 4. Although the amount of leachate added to each column was similar, there are obvious variations among the soils. Copper was extracted from Wagram loamy sand as deep as 6 cm, but from Fanno silty clay only as deep as 3 cm (Figure 3). Soil texture and its consequent effects on flow obviously play a significant role in the migration of Cu and Pb. Had the soil columns been leached long enough, the effect of soil properties on migration of Cu and Pb could have been shown by monitoring the effluent as was done for other divalent cations. These results suggest that the behavior of Cu and Pb could be added to Cd, Ni, Be, and Zn as divalent cations whose movement is best estimated by knowledge of surface area, clay content, and the content of free iron oxides.

Relatively large quantities of sorbed material were extracted by the 0.1 N HCl. All of the attenuated ion was removed in some instances (Table 2). Cd, Zn, and Ni were easiest to extract. Furthermore, the more coarse textured the soil, the greater the efficiency of extraction, since the most effective extractions were with the sandy soils--Anthony, Kalkaska, Mohave and Wagram. The amount of sorbed Cd removed by acid extraction for these four soils ranged from 90 to 100%. For clay soils such as Davidson, Nicholson, Fanno, and $\text{Mohave}_{\text{Ca}}$, the efficiency was 70 to 80%.

Water Extractions

The order of extractability with water

Table 2. THE AMOUNT OF SORBED TRACE ELEMENT EXTRACTED BY 0.1 N HCl

Soils	Trace Element								
	As	Cd	Cr	Cu	Hg	Ni	Pb	V	Zn
					%				
Wagram l.s.	11	90	8	60	14	100	41	100	100
Ava s.c.l.	11	85	7	40	16	72	78	75	64
Kalkaska s.	18	100	16	67	31	100	70	48	100
Davidson c.	5	77	7	67	49	43	70	36	42
Molokai c.	0	87	5	57	59	78	59	35	100
Chalmers s.c.l.	nd	nd	nd	nd	22	57	nd	80	nd
Nicholson si.c.	11	75	13	27	24	63	47	55	64
Fanno c.	24	80	8	44	17	58	58	89	66
Mohave s.l.	11	89	7	55	30	80	77	93	100
Mohave_{Ca} c.l.	20	74	17	51	59	31	57	77	41
Anthony s.l.	13	100	100	68	23	100	93	63	100

nd = not determined

was much different than with acid: V > Se > As ≥ Cr > Zn > Ni > Cd > Hg > Cu > Pb. Although this order is highly empirical the trend is that elements sorbed as anions are most susceptible to leaching by water. These results support the work of Jacobs, Syers, and Keeney (1970) whose data suggest that in soils having a low As sorption capacity, a portion of the As is readily mobile.

The percentage of sorbed ion extracted by water can vary by an order of magnitude. Total amounts extracted, however, were very low (Table 3), usually <3% of the total adsorbed. Virtually all of the ion was released from the top ten percent of the soil column. Thus, the percent extracted does not reflect the potential for migration of the ions because the ions could be re-adsorbed as they were moved down the column. The implication is that leaching with water would not cause serious desorption of attenuated ions. Of course, these data give no clue to the effects of redox potential.

Figure 5 shows that the relative efficiency of the acid versus the water extraction is not constant throughout the column. This was true in every case studied. Total analyses performed on a few of the columns confirmed that the efficiency of extraction decreased with column depth. However, the effectiveness of extraction with water decreased much faster than with acid. These results suggest the presence of more than one attenuation mechanism and that the material initially adsorbed by the soil is the most strongly held.

These data should primarily be viewed as preliminary and be utilized only as a point of departure for future research. Clearly, questions with respect to redox potential and the effects of extracts with higher organic matter content have not been answered. Where time and facilities permit, an improved method of studying "leaking" would be by leaching the soil columns successively with a waste stream, then with water or other leachates.

Solution Flux

In the initial leaching work in this laboratory the migration of Cr was most susceptible to changes in leaching rate. Therefore, the effect of three flow rates of 60 ppm Cr through Kalkaska sand was examined and the results are shown in Figure 6. These data were obtained with the constant flow pump and fraction collector. The most evident manifestation of the effect of flux is a comparison of the point at which initial detection occurred. With both of the faster rates, Cr appeared in the effluent prior to the leaching of three pore volumes. With the slower rate, it was not until 15 pore volumes were leached that Cr was detected in the effluent. A similar situation is shown in Figure 7 with Cr and Fanno clay.

To date three soils have been examined in this manner for Cr and Cd. The results have not been as dramatic, as shown in Figure 8, with 100 ppm Cd and Davidson clay. Initial detection of Cd was delayed for the slower rates but the differences are rather small.

Although these data concerning the effect of flux are also preliminary, the potential has been shown that studies of this type may yield valuable information in terms of site selection and water management of landfills.

The need for other experiments is suggested by this preliminary work. For instance, it would be important to know whether the additional material attenuated at slow flow rates is as tightly retained. These measurements may lead to additional work in terms of measuring reaction rates and elucidating mechanisms of attenuation.

CREDITS

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Table 3. THE AMOUNT OF SORBED TRACE ELEMENT EXTRACTED BY DEIONIZED WATER

	Trace Element									
	As	Cd	Cr	Cu	Hg	Ni	Pb	Se	V	Zn
	%									
Wagram l.s.	0	9	0	0.5	1.6	7	0	1.7	9	8
Ava si.c.l.	3	5	2	0.3	0	6	0.7	5	0	5
Kalkaska s.	2.5	2	0.5	0.5	0	18	0.3	9	7.5	5
Davidson c.	0.5	1	4	1.5	2.2	1	0	3	0.4	3
Molokai c.	0	0.5	1	0.1	0	1.1	0	3	0.7	2
Chalmers si.c.l.	nd	nd	nd	nd	0.5	3	nd	nd	3.8	nd
Nicholson si.c.	2	1	10	0	0	0.2	0.2	0.5	1.5	1
Fanno c.	4.5	1	1	3	0.5	2	0.2	0	8	1.2
Mohave s.l.	0	2	0	0.5	0	4	0.4	3	0.3	2.5
Mohave$_{Ca}$ c.l.	11.5	0.2	6	0.2	0	0.1	0.1	6	23	0.1
Anthony s.l.	0	3.5	0	3	9	18	0	1.8	28	2.8

nd = not determined

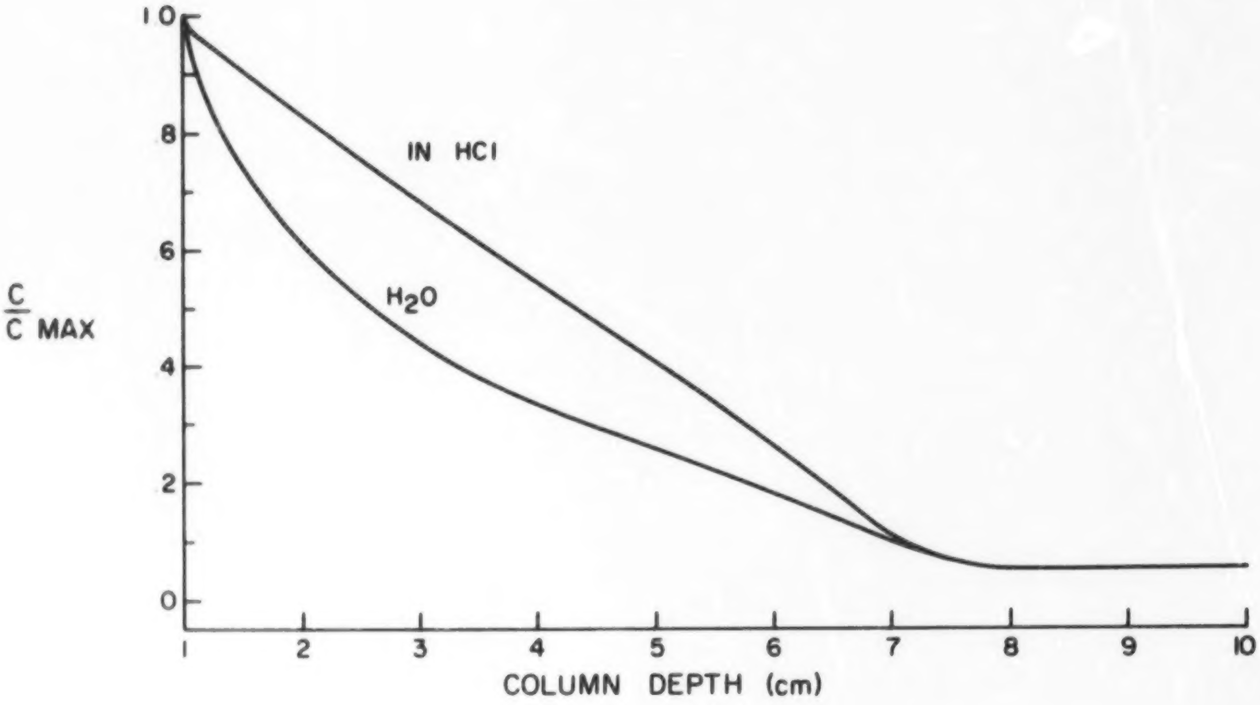

Figure 5. Extraction of Ni from Fanno clay.

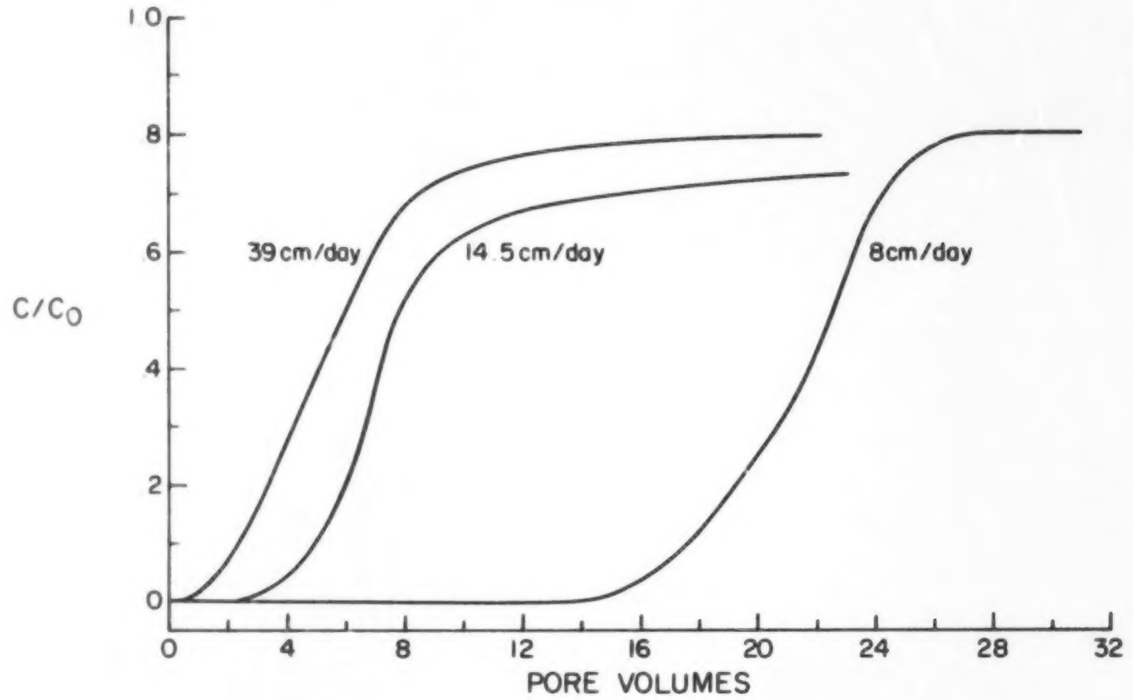

Figure 6. Migration of Cr through Kalkaska sand as related to leaching rate.

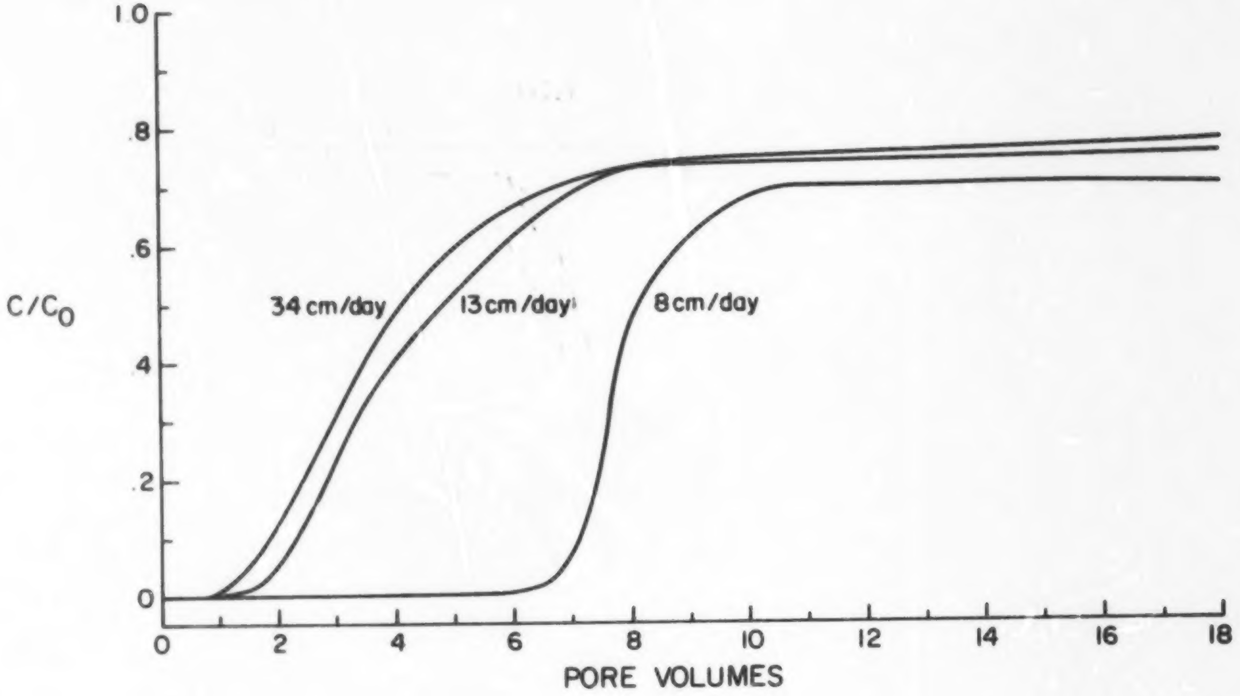

Figure 7. Migration of Cr through Fanno clay as related to leaching rate.

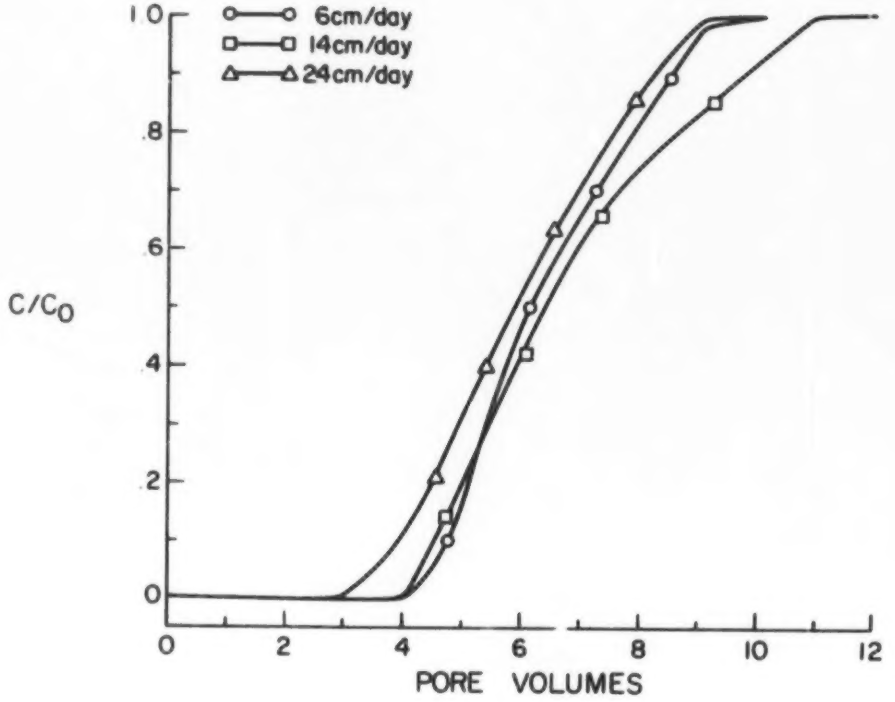

Figure 8. Migration of Cd through Davidson clay as related to leaching rate.

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EFFECT OF pH ON REMOVAL OF HEAVY METALS FROM LEACHATES BY CLAY MINERALS

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ABSTRACT

The potential usefulness of clay materials as liners for waste disposal sites depends to a large extent on the pH of the leachate solutions that pass through the landfill and on ionic competition during the ion adsorption process. Adsorption of the cationic heavy metals—Pb, Cd, Zn, Cu, and Cr(III)—was found to increase as the pH increased, while adsorption of the anionic heavy metals—Cr(VI), As, and Se—decreased as the pH increased. The presence of leachate reduced the amounts of the cationic heavy metals removed from solution by as much as 85 percent, whereas leachate had a relatively minor effect on the amounts of the anionic heavy metals removed by the clays. It was concluded that removal of the heavy-metal cations from solution is primarily a cation exchange-adsorption reaction that is affected by pH and ionic competition, whereas removal of the heavy-metals anions is primarily an anion-adsorption reaction in which the monovalent ion is the one being predominantly adsorbed. Precipitation of the heavy-metal cations in leachate was found to be an important attenuation mechanism at pH values of 5 and above. No precipitation of the heavy-metal anions was detected in the pH range 1.0 to 9.0. Adsorption isotherms determined at various pH values were used to compute how thick a clay liner must be to remove Pb from solutions of $Pb(NO_3)_2$, from 0.1 M NaCl, and from two landfill leachates at concentrations ranging between 10 and 1000 ppm Pb and at pH values from 3 to 8. Where pH and ionic competition are unfavorable, some undesirable environmental consequences of heavy-metal adsorption reactions can occur.

INTRODUCTION

As industry in the United States complies with the Clean Air Act and the Federal Water Pollution Control Act, it finds itself obliged to handle and dispose of huge volumes of solid wastes, sludges, and liquid concentrates of pollutants. With traditional disposal methods outlawed, the quantity of industrial wastes that must be placed in landfills is expected to double in the next 10 years. The U.S. Environmental Protection Agency (1) estimates that about 10 percent of the nonradioactive industrial wastes will be classified as hazardous and will therefore require special landfill sites and disposal precautions.

While the volumes of industrial wastes are doubling in the next 10 years, the amount of land available for industrial waste disposal will be declining. In Illinois, the Illinois State Geological Survey has for the past 15 years assisted the regulatory agencies by evaluating the hydrogeologic conditions at proposed or operating waste disposal sites. During the past 5 years the Survey has appraised conditions relative to pollution hazard for about 300 sites annually. Our experience indicates that acceptable disposal sites will be difficult to find in the future. Their establishment will be approved only after certain geologic and hydrologic criteria are met and their operation will be required to be environmentally acceptable.

The relative unavailability of geologically acceptable sites close to industrialized areas and the rapidly escalating costs associated with transportation of waste materials across long distances now make it economically feasible to consider physical modifications of sites heretofore geologically unacceptable that may be ideal in other respects. Sufficient studies (e.g., see 2) have been made to establish that pollutants are attenuated by passage through earth materials. It has therefore been suggested (2) that a clay liner in the bottom of otherwise unacceptable sites, such as gravel pits or old quarries, could make them acceptable for disposal of municipal and/or industrial wastes. However, no sound evidence was available to indicate how thick such a layer must be or what types of clay minerals would be best suited for removal of toxic metals in the presence of the leachates that would be encountered in the landfill.

This paper reports an overview of results obtained at the Illinois State Geological Survey during an investigation that was supported in part by U.S. Environmental Protection Agency contract No. 68-03-0211, Cincinnati, Ohio. The complete results were presented in the final report for that contract (3). One purpose of the portion of the investigation reported here was to determine the capacity of two major types of clay minerals for removing the potentially hazardous heavy metals—As, Cd, Cr, Cu, Hg, Pb, Se, and Zn—from solution. The effect landfill leachates have on this capacity at various pH values also was determined. Another purpose was to gain insight into the mechanisms responsible for attenuation of the various heavy metals and the relative mobilities of the metals through clay materials. We also wished to evaluate the potential usefulness of clay minerals as liners for waste disposal sites.

EXPERIMENTAL

The research was conducted in the Environmental Geology Laboratory of the Illinois State Geological Survey. The clays used in the study were the purified clay minerals kaolinite and montmorillonite. These particular clays were chosen because they closely represent clay minerals commonly found in soils and because they are obtainable in commercially available quantities. The details of the clay mineralogy, purification procedures, and chemical analyses are available in the final report to EPA (3).

The municipal leachates used in this study were collected from the Du Page County landfill and from the Blackwell Forest Preserve landfill, both in northeastern Illinois. Details of the site locations and sampling procedures also are given in the final report to EPA (3). The results of chemical analyses of the leachates are reported in Table 1. For comparison, Table 1 also contains a summary of the range of leachate characteristics found for more than 20 other leachates by Garland and Mosher (4).

The details of the experimental procedures used for the heavy-metal adsorption studies were given in our final report to EPA (3). In general, the studies were conducted by placing a known weight of clay in a flask containing a known volume of the solution of interest. The pH values of replicate suspensions were adjusted with either HNO_3 or NaOH over the pH range 1 to 9. The suspensions were then shaken in a constant temperature bath at 25°C, the equilibrium pH was recorded, the samples were centrifuged, and the solutions were analyzed for their metal concentrations. The difference between the initial concentration and the equilibrium concentration was used to compute the amount of metal removed from the solution at the particular pH by a given clay mineral. This procedure was carried out for a range of initial metal ion concentrations that varied between 10 and 1000 ppm.

RESULTS AND DISCUSSION

The results reported here are an overview of the detailed final report written in fulfillment of EPA contract 68-03-0211. More complete information concerning the topics presented can be attained by requesting a copy of the final report from the author.

Cationic Heavy-Metal Adsorption

During preliminary experiments on Cr(III) adsorption by kaolinite, the removal curves shown in Figure 1 were obtained. These curves illustrate the important effect pH has on the removal of cationic Cr(III) species from solutions of $Cr(NO_3)_3$ and Du Page leachate. A marked reduction in Cr(III) removal due to the presence of leachate is also shown in Figure 1. This reduction in removal was observed for all the cationic heavy metals studied (Cr(III), Pb, Cu, Zn, and Cd). The curve labeled "blank" in Figure 1, representing removal of Cr(III) from

TABLE 1. SUMMARY OF CHEMICAL CHARACTERISTICS OF LANDFILL LEACHATES
(from Griffin and Shimp (3))

Component	Range of all values from Garland and Mosher (4) (mg/1)	Blackwell Forest Preserve leachate data from Hughes (2) (mg/1)	Du Page leachate used in sorption study (mg/1)
COD	40 to 89,520	39,680.	1,362.
BOD	9 to 54,610	54,610.	—
TOC	256 to 28,000	—	—
Organic acids	—	—	331.
Carbonyls as acetophenone	—	—	57.6
Carbohydrates as dextrose	—	—	12.
pH	3.7 to 8.5	7.10	6.73
Eh (m.v.)	—	-182.	-155.
TS	0 to 59,200	—	—
TDS	0 to 42,276	19,144.	5,910.
TSS	6 to 2,685	—	—
E.C. (mmhos/cm)	2 to 17	10.90	7.20
Alkalinity ($CaCO_3$)	0 to 20,850	7,255.	4,325.
Hardness ($CaCO_3$)	0 to 22,800	7,830.	1,100.
Total P	0 to 154	6.	< 0.1
Ortho P	6 to 85	—	—
NH_4-N	0 to 1,106	—	809.
NO_3+NO_2-N	0 to 1,300	1.70	—
Al	—	2.25	< 0.1
As	—	4.71	0.11
B	—	—	33.
Ca	5 to 4,080	—	49.
Cl	34 to 2,800	1,697.	1,070.
Na	0 to 7,700	900.	522.
K	3 to 3,770	—	516.
Sulfate	1 to 1,826	680.	< 0.01
Mn	0 to 1,400	1.66	< 0.1
Mg	16 to 15,600	—	204.
Fe	0 to 5,500	5,500.	4.40
Cr	—	0.20	< 0.1
Hg	—	—	0.0008
Ni	—	—	0.5
Si	—	—	15.1
Zn	0 to 1,000	—	0.03
Cu	0 to 10	0.05	< 0.1
Cd	0 to 17	< 0.05	< 0.01
Pb	0 to 5	—	< 0.1

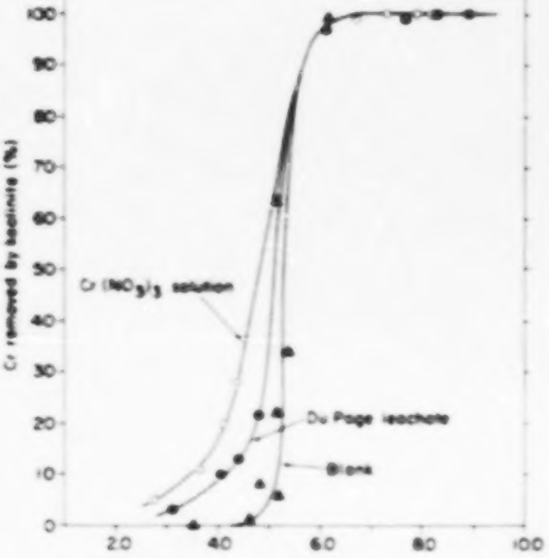

Figure 1. Removal of Cr(III) from solution by kaolinite. The curve labeled "Blank" represents a $Cr(NO_3)_3$ solution without kaolinite.

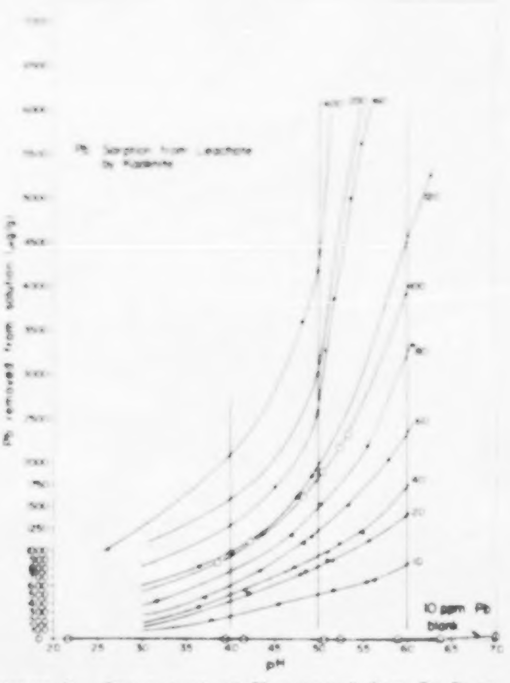

Figure 2. The amount of Pb removed from Du Page leachate by kaolinite at 25°C plotted as a function of pH. Initial Pb concentrations (ppm) are indicated beside each curve.

a solution containing no clay, shows that precipitation becomes a very important mechanism of Cr(III) removal near pH 5 and above. The precipitate formed in these experiments was collected and identified by its color and X-ray diffraction pattern as hydrated chromic hydroxide.

The results of heavy-metal removal from 25°C solutions of Du Page leachate by kaolinite and/or montmorillonite were plotted as a function of pH for Pb in Figure 2, for Cu, Zn, and Cd in Figure 3, for Cr(VI) in Figure 4, for Se in Figure 5, and for As(V) in Figure 6. The data indicate that removal of the heavy-metal cations from landfill leachate generally increases with increasing pH values and with increasing concentration of the metal ion in solution. As was true for the Cr(III) data shown in Figure 1, the sharp rise in removal in the pH range 5 to 7 is due to precipitation of various insoluble hydroxide and carbonate compounds, depending on the pH and the particular ion in question. In sharp contrast is the data for the anionic heavy metals (Cr(VI), Se, and As), which show a general decrease in removal as the pH is raised. In addition, no precipitation of the anionic heavy metals was observed over the pH range 1 to 9.

When data for heavy-metal removal from leachate are plotted as a family of curves of increasing concentration, as shown in Figures 2 through 6, sorption isotherms may be constructed from the plot for any desired pH value within the range given in the plot. A sorption isotherm can easily be constructed from these plots by placing a vertical line across the family of curves at the pH of interest. Figure 2 gives an example at pH values 4, 5, and 6. The amount of metal ion removed from solution is found on the graph at the points where the vertical pH line intersects each curve. The equilibrium ion concentrations that correspond to the chosen pH value are then computed from the initial concentrations (shown beside each curve) and the amounts removed from solution at each concentration. A more complete description and examples of the calculation were presented by Griffin and Shimp (3).

Sorption isotherms were constructed by this method for several pH values from the plots given in Figures 2 through 6. A representative isotherm computed for Pb from Figure 2 at pH 5.0 is presented in Figure 7

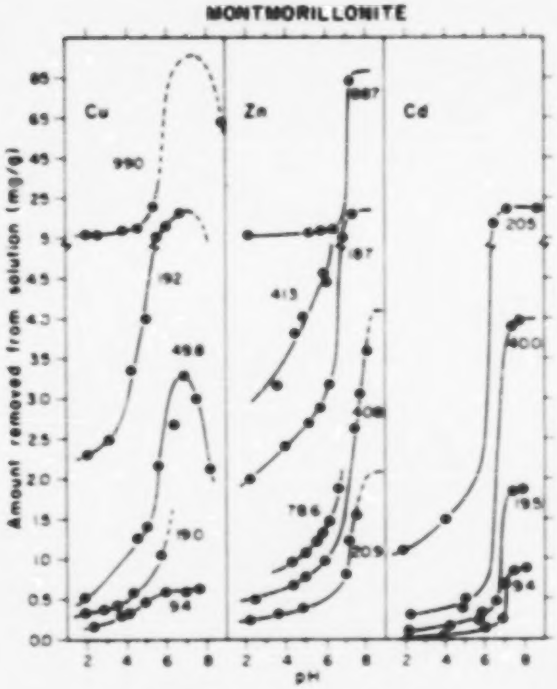

Figure 3. The amount of Cu, Zn, or Cd removed from Du Page leachate solutions by montmorillonite at 25°C, plotted as a function of pH. The plots are labeled with the initial solution concentration (ppm) of Cu, Zn, or Cd from which each plot was obtained.

along with sorption isotherms obtained at pH 5.0 for Pb sorption from Blackwell leachate, pure $Pb(NO_3)_2$ solutions, and 0.1 M NaCl solutions containing added $Pb(NO_3)_2$. The results indicate that maximum Pb sorption occurred in pure $Pb(NO_3)_2$ solutions, with decreasing sorption in the 0.1 M NaCl solutions, a further decrease in the Du Page leachate, and the greatest decrease in Blackwell leachate.

The sorption isotherms for the two leachates show a sharp upswing occurring at equilibrium concentrations of approximately 200 ppm Pb. A sharp upswing in a sorption isotherm at higher concentrations is generally viewed as initiation of precipitation of an insoluble compound. A white precipitate was observed forming in the leachate solutions and was identified by its X-ray diffraction pattern as a highly crystalline $PbCO_3$.

The sorption maximums of Pb in pure $Pb(NO_3)_2$ solutions, determined from sorption isotherms such as that shown in Figure 7, for kaolinite and montmorillonite are, respectively, 15.36 and 79.56 meq Pb^{++}/100 g clay. These values are comparable to the cation exchange capacity (CEC) values of 15.1 for kaolinite and 79.5 meq/100 g for montmorillonite that were determined experimentally. The CEC values are within 2 percent of the Pb sorption maximums determined from the sorption isotherm—i.e., Pb^{++} sorption is merely another method of measuring the cation exchange capacity of a clay. This is taken as evidence that cation exchange is the principal mechanism of Pb sorption. More evidence comes from the fact that, for each of the heavy-metal cations studied, montmorillonite adsorbed five times more metal ion than kaolinite. This five-fold increase is the ratio of their respective CEC values.

Other evidence in support of a cation exchange mechanism is the reduction in Pb sorption from solutions containing 0.1 M NaCl and from the two leachates (Figure 7). The decrease in Pb sorption is attributed to increasing competition for cation exchange sites by Na^+ in the 0.1 M NaCl solutions and to an increase in the divalent cation competition in the two leachates. The Blackwell leachate has a much higher total salt content than the Du Page leachate, and the high concentrations of competing ions could account for the greatly reduced Pb sorption in landfill leachate compared to the sorption in pure $Pb(NO_3)_2$ solutions.

The results of the above studies with Pb, similar results for Cr(III), Cu, Zn, and

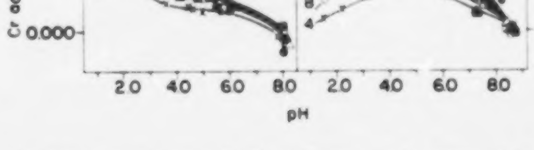

Figure 4. Chromium (VI) adsorption-pH curves for kaolinite at 25°C. Initial Cr(VI) concentrations (ppm) are indicated beside each curve.

Cd, and the evidence from other supporting studies (3), have led to the conclusion that the removal of the heavy-metal cations from strongly acid solutions by clay minerals is primarily an exchange-adsorption reaction that is affected by ionic competition. As the pH is raised, adsorption is increased due to reduced competition from H^+ and formation of a series of hydroxyl complex ions of lower valence. Finally, initiation of precipitation occurs in the pH range 5 to 7 and precipitation becomes the major removal mechanism in the neutral and alkaline pH range. All of the heavy-metal cations studied followed this pattern. However, the amounts removed and the pH at which precipitation was initiated varied with the individual element (Figures 1, 2, and 3).

Anionic Heavy-Metal Adsorption

The data for Cr(VI) removal from solutions of K_2CrO_4 and Du Page leachate (Figure 4) are in sharp contrast to the data for the cationic heavy metals presented above. The

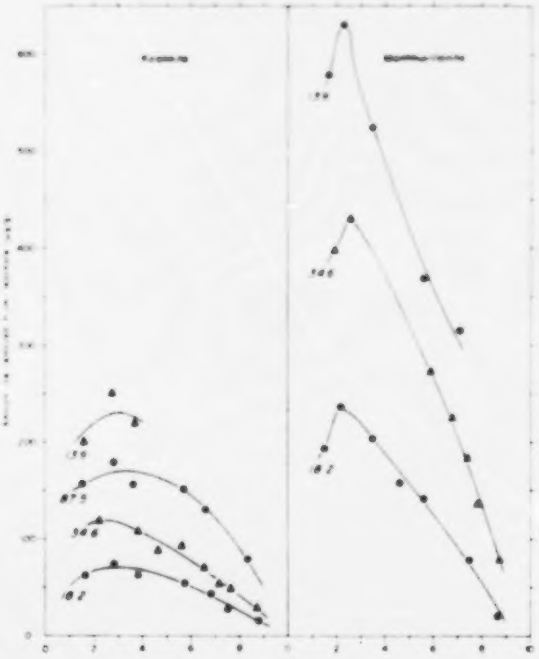

Figure 5. The amount of Se(IV) removed from Du Page leachate solutions by kaolinite and montmorillonite at 25°C plotted as a function of pH. Labels are the initial solution concentration of Se(IV) in ppm.

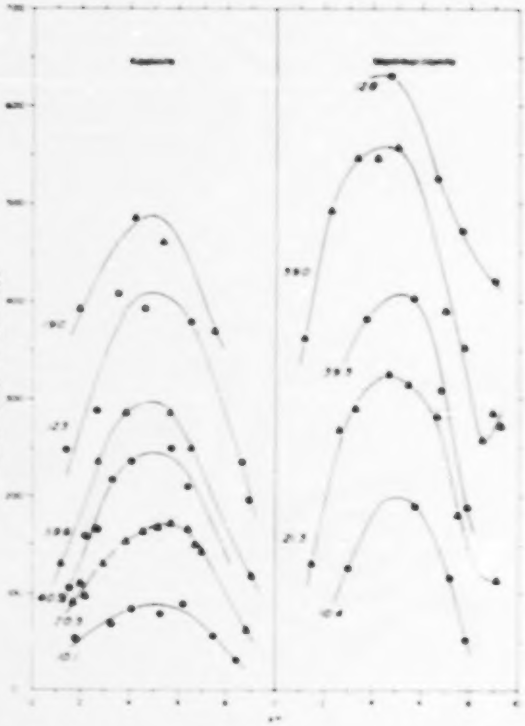

Figure 6. The amount of As(V) removed from Du Page leachate solutions by kaolinite and montmorillonite at 25°C plotted as a function of pH. Labels are the initial solution concentration of As(V) in ppm.

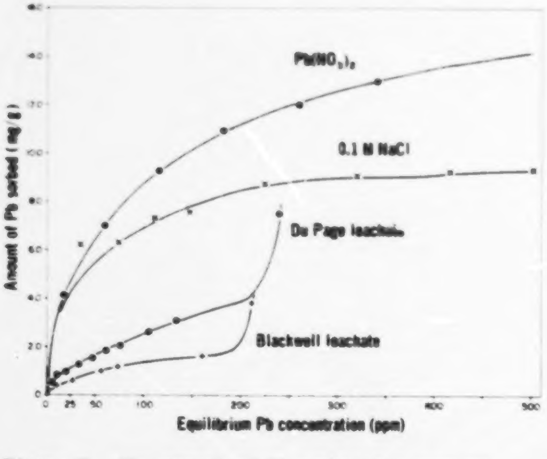

Figure 7. The amount of Pb sorbed per gram of kaolinite at pH 5.0 and 25°C plotted as a function of the equilibrium Pb concentration.

most striking difference is that sorption is reduced as the pH is increased. An important point to note is that sorption actually goes to zero at approximately pH 8.4. A second major difference is that sorption is greater from leachate than from pure K_2CrO_4 solutions. Other major differences, not obvious from the figure, are the absence of precipitation in the pH range 1 to 9 and the small amounts removed from solution compared to the results for cationic heavy metals. The differences make it clear that the sorption and removal mechanism for the anionic heavy metals (Cr(VI), Se, and As) is quite unlike the mechanism for the cationic heavy metals.

Diagrams showing the distribution of Cr(VI) species in solution as a function of pH were constructed to aid in interpretation of the data. The principal species in solution throughout the pH range of maximum adsorption was the $HCrO_4^-$ ion. The diagram showed that the fraction of $HCrO_4^-$ ions in solution begins at pH 5 to decrease rapidly, reaching zero at pH 8.4. The principal species present in solution at pH values above 8.4 is CrO_4^{2-}. Below pH 2, the fraction of $HCrO_4^-$ ions decreases rapidly as the fraction of H_2CrO_4 species increases.

The behavior of the Cr(VI) adsorption-pH curves in Figure 4 implies that the $HCrO_4^-$ ion is the principal ion being adsorbed by the clay minerals. Conversely, the lack of adsorption at pH values above 8.5 indicates that the CrO_4^{2-} ion is completely unadsorbed by the clay. Apparently the divalent anion species is repelled by the net negative charge on the clay surface.

For both clay minerals, more Cr(VI) was adsorbed from Du Page leachate solutions than from pure K_2CrO_4 solutions throughout the pH range 3 to 7. Evidently, anions (e.g., Cl^- and HCO_3^-) in the leachate do not compete favorably with $HCrO_4^-$ ions, or adsorption would have decreased. The higher adsorption in leachate may result from formation of organic or inorganic polynuclear complexes in the leachate solution that can be adsorbed by the clay.

Similar results have been obtained for the clay mineral adsorption of Se(IV) and As(V) species from leachate (Figures 5 and 6). Although the data are not as complete as those for Cr(VI) adsorption, the Se data shown in Figure 5 apparently converge on zero adsorption at approximately pH 10. As was true for Cr(VI), this result corresponds to the point in the Se(IV) species distribution at which the monovalent $HSeO_3^-$ ion goes to zero and the SeO_3^{2-} ion emerges. At pH values below 3, H_2SeO_3 is the principal species in solution, and the $HSeO_3^-$ ion decreases rapidly. This pattern corresponds to the sharp decrease in Se adsorption at pH values less than 3 shown in Figure 5.

Results similar to those for Cr(VI) and Se(IV) species are shown for As(V) species in Figure 6. It is noteworthy that the amount of As(V) species removed from solution reaches a maximum at about pH 5. Comparison of the distribution of As(V) species in solution as a function of pH reveals that the As(V) removal curves follow the monovalent $H_2AsO_4^-$ species distribution curve almost exactly. It was therefore concluded that the monovalent $H_2AsO_4^-$ ion is the principal species being adsorbed by the clay minerals, a conclusion similar to those reached for Cr(VI) and Se(IV).

The results of this study indicate that pH has a pronounced effect on the amounts of Cr(VI), Se(IV), and As(V) adsorbed from solutions by clay minerals. It was concluded that the principal adsorption mechanism is anion exchange and the species distribution diagrams led us to believe that the adsorption was due principally to the monovalent species of each element studied, which led to the strong pH dependency of the adsorption process. The precise mechanism for anion adsorption by clay minerals is not known but we conclude, as others have, that anion exchange plays an important role in the adsorption process.

A comparison of the relative amounts of heavy metals removed at pH 5.0 from 100 ppm equilibrium concentration solutions of the metals studied, both cationic and anionic, is presented in Table 2. The table indicated that the cationic heavy metals are generally adsorbed to a greater degree than the anionic forms. However, this ranking is somewhat pH dependent since the greatest anion adsorption occurs in acid solutions and the greatest cation adsorption in alkaline solutions. Thus, the ranking changes somewhat at different pH values.

A significant point shown in Table 2 is the importance of the valence state of an element to the amount of that element

TABLE 2. REMOVAL OF HEAVY METALS FROM SOLUTIONS BY KAOLINITE AT pH 5.0

Element	Amount removed at 100 ppm equilibrium concentration (micromoles/g) Pure solutions	Amount removed at 100 ppm equilibrium concentration (micromoles/g) Du Page leachate
Cr (III)	769*	576*
Cu	55.1	15.7
Pb	42.3	12.1
As (V)	†	5.3
Zn	33.6	3.8
As (III)	‡	2.0
Cd	26.7	1.9
Cr (VI)	0.62	1.9
Se	†	1.9

* Precipitation contributes to removal at pH 5.0.

† Removals from 40 ppm solutions were approximately the same as removals from leachate.

‡ Removals from 40 ppm solutions were 30 percent greater than from removals from leachate.

removed from solution by clay minerals, Cr(III) species are removed to a much greater extent than Cr(VI) species. Studies showed that the clay minerals removed 30 to 300 times more Cr(III) from solution than Cr(VI). The table also shows the more extensive removal of As(V) than As(III). These results indicate that safer disposal of certain elements may be achieved by conversion of the element, prior to deposition at the landfill or disposal site, to the form that would be most strongly attenuated.

Application of Data to Site Design

An example of how data from the study can be used is its application to the question posed at the beginning of the paper—how thick a proposed clay liner must be to remove a specific heavy metal from a landfill leachate or industrial waste stream. Lead is used here as an example.

From a family of adsorption-pH curves, such as those in Figure 2, adsorption isotherms for a given pH solution can be constructed—for example, the Pb isotherms constructed at pH 5.0 shown in Figure 7. The amount of Pb that will be removed from a pH 5.0 solution of given concentration by one gram of kaolinite clay can be read directly from the graph or computed by fitting an equation to the data. Therefore, if the amount of Pb and the pH of the solution are known, the thickness of clay necessary to remove it from solution can easily be calculated. Conversely, if the thickness of clay is given, then the volume at which the Pb will saturate the adsorption capacity and break through the liner also can be easily computed. However, this approach assumes equilibrium conditions exist and also that dispersion and diffusion are negligible. Such ideal conditions seldom exist during dynamic flow through a porous media.

To determine the validity of using adsorption isotherms to predict the thickness of a clay liner, leaching experiments were carried out in laboratory columns. A column containing quartz sand mixed with a known weight of kaolinite was leached with pH 5.0 Du Page leachate containing 100 ppm Pb added as $Pb(NO_3)_2$. Analysis of the column effluent for Cl^- and Pb^{++} were carried out on 5 ml effluent fractions collected with an automatic fraction collector. The volume at which Pb breakthrough would occur was computed from the data plotted in Figure 7. The results are shown in Figure 8. Chloride is assumed to be a non-interacting ion, and its breakthrough pattern gives a relative idea of the dispersion component of the column. A slow flow rate of approximately 0.4 ml/min was used so that the assumption of equilibrium conditions was closely approximated. The results shown in Figure 8 indicate that the actual Pb breakthrough closely approximated the predicted Pb breakthrough curve. Comparison of the Pb and Cl data points indicates that deviations between the "actual" and "predicted" curves were largely caused by dispersion.

A second column containing a known weight of clay in a clay-sand mixture was leached with a fixed volume of solution. The solution contained 100 ppm Pb in a 0.1 M NaCl matrix. The solution was adjusted to pH 5.0 and a known volume added to the top of the column. The depth of Pb penetration in the column was predicted by using the data for Pb adsorption from NaCl solutions given in Figure 7. After the column had drained freely, the contents were cut into sections and analyzed for their Pb content. The results are shown in Figure 9. The

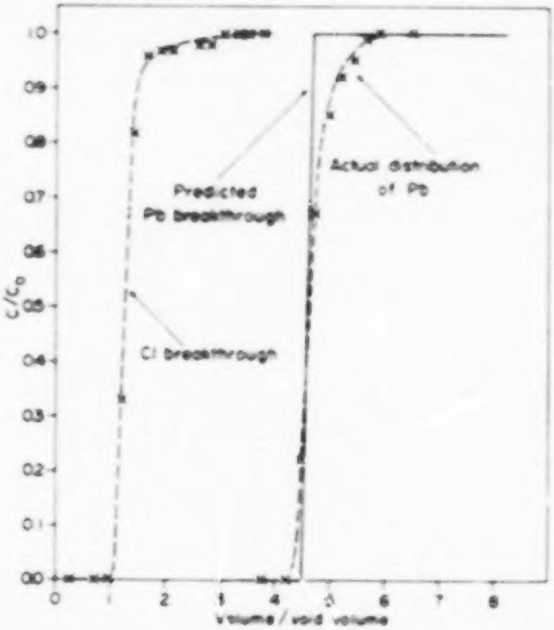

Figure 8. Predicted and actual breakthrough curves for a column leached with Du Page leachate with 100 ppm added Pb and containing 2 percent kaolinite mixed with sand.

predicted depth of Pb migration closely approximated the actual distribution of Pb in the column.

A better prediction could undoubtedly be achieved if the effect of dispersion were included. However, the simplistic approach used here may give sufficiently accurate estimates of the necessary clay depth for many purposes without the expense of computer-implemented calculations. The results of computations of the thickness of clay liners necessary for removal of Pb from solutions of various compositions are given in Table 3.

Table 3 shows how thick a square meter of a 30 percent clay liner, packed to a bulk density of 1.60 g/cc, need be to remove all the Pb from 762 liters (201 gal) of solution. This particular volume is the amount generated from a typical sanitary landfill containing municipal solid waste placed 3 meters (10 feet) deep and having an annual net infiltration of 254 mm (10 inches) (5). The thicknesses of the clay liner given in the table, therefore, effect total removal of Pb for *one year* by a square meter of liner at the given concentrations of Pb and pH values. They are, of course, the minimum thicknesses possible, since they represent an idealized situation. The actual thickness necessary in a field application must be somewhat greater to allow for nonequilibrium conditions, physical dispersion, diffusion, and the normal engineering safety factors.

The information in Table 3 indicates that only relatively thin layers of clay, especially montmorillonite, are necessary for removal of Pb unless the pH values are very acid and the Pb concentrations are high. The high sorption capacity of clay minerals and the reversible nature of exchange adsorption reactions have important environmental consequences. Soils and

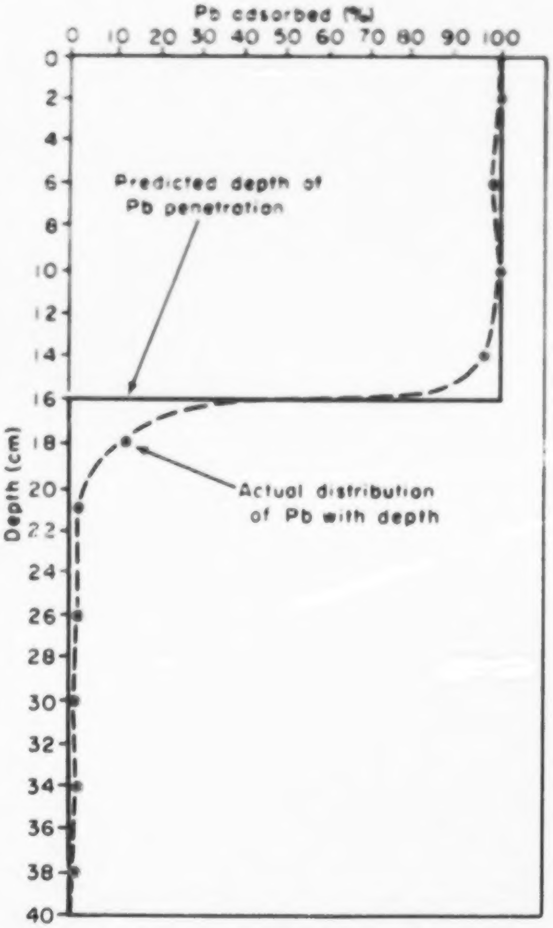

Figure 9. Predicted and actual distribution of Pb with depth in a column leached with 0.1 M NaCl with 100 ppm Pb added and containing 2 percent kaolinite mixed with sand.

TABLE 5. THICKNESS (cm) OF A SQUARE METER OF A 30% CLAY LINER NEEDED TO REMOVE Pb FROM 762 LITERS (201 GALLONS) OF SOLUTION PER YEAR

	10 ppm Pb at pH			100 ppm Pb at pH			1000 ppm Pb at pH		
	3	5	8	3	5	8	3	5	8
KAOLINITE									
$Pb(NO_3)_2$	—	< 1	—	5.3	1.8	< 1	—	10.0	—
0.1 N NaCl	—	< 1	—	—	2.3	—	—	13.2	—
Du Page	15.9	2.1	•	28.9	6.4	•	79.4	•	•
Blackwell	19.8	4.0	•	49.6	11.3	•	264.6	•	•
MONTMORILLONITE									
$Pb(NO_3)_2$	—	< 1	—	—	< 1	—	—	1.9	—
Du Page	9.9	1.8	•	15.2	3.7	•	18.0	•	•

• Precipitation as $PbCO_3$.

surface waters may change in ionic composition or pH as environmental conditions change. A sudden decrease in pH may release large amounts of potentially toxic Pb into the aqueous phase, especially in places where $PbCO_3$ has accumulated. Cations, especially di- and tri-valent, compete with Pb and may exchange with it, thus allowing Pb to come into solution. These multiple interactions must be considered when a disposal site is designed and the environmental impact of Pb and other heavy metals assessed.

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